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of the
SOCIETY OF DYERS AND COLOURISTS

Volume 70 Number 3

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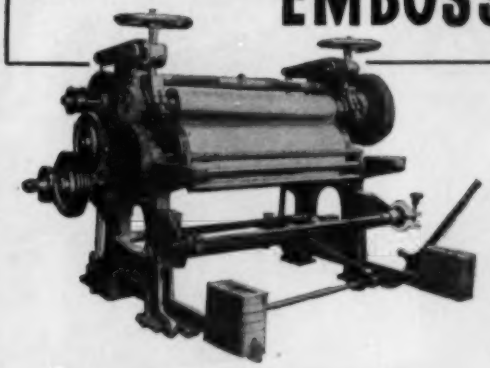

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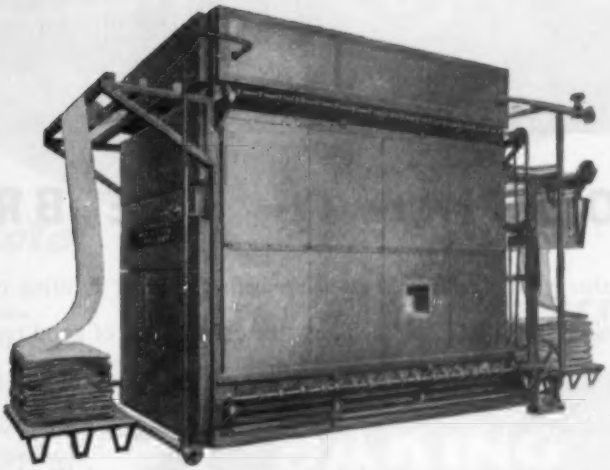

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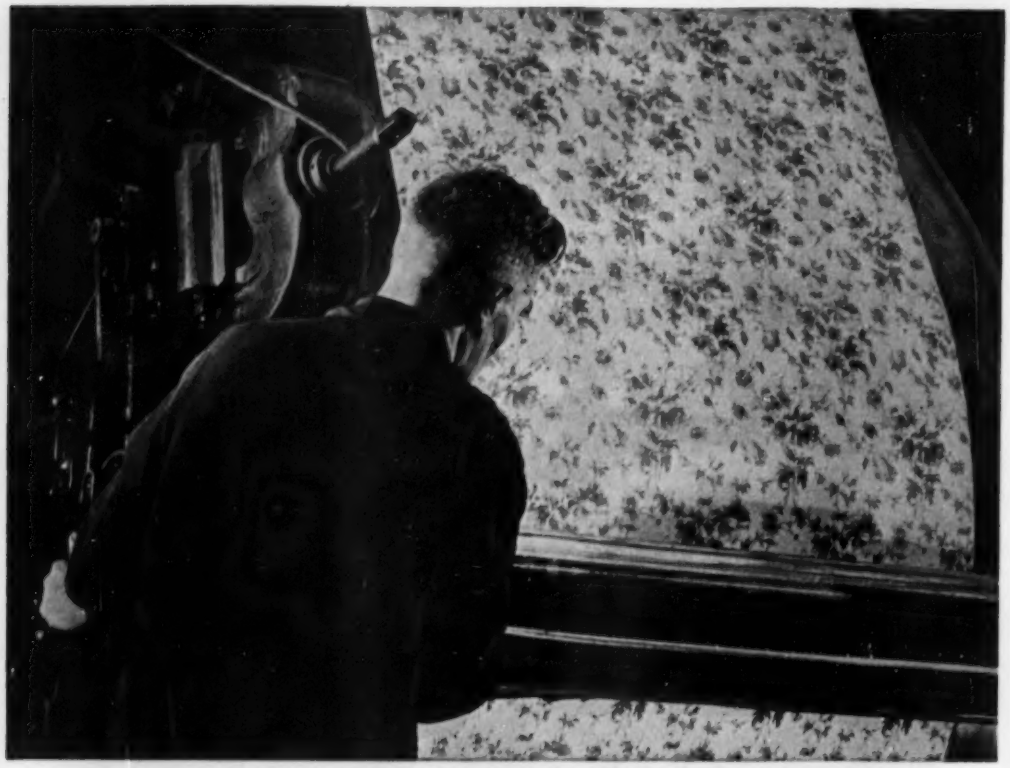

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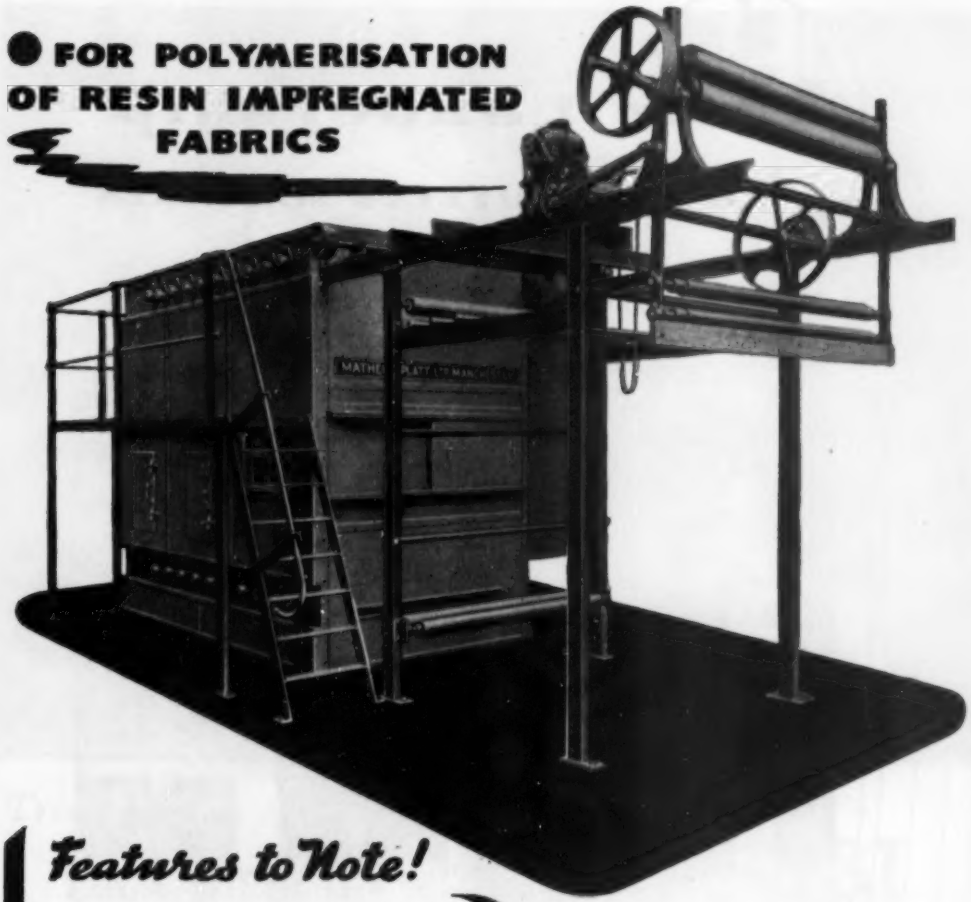

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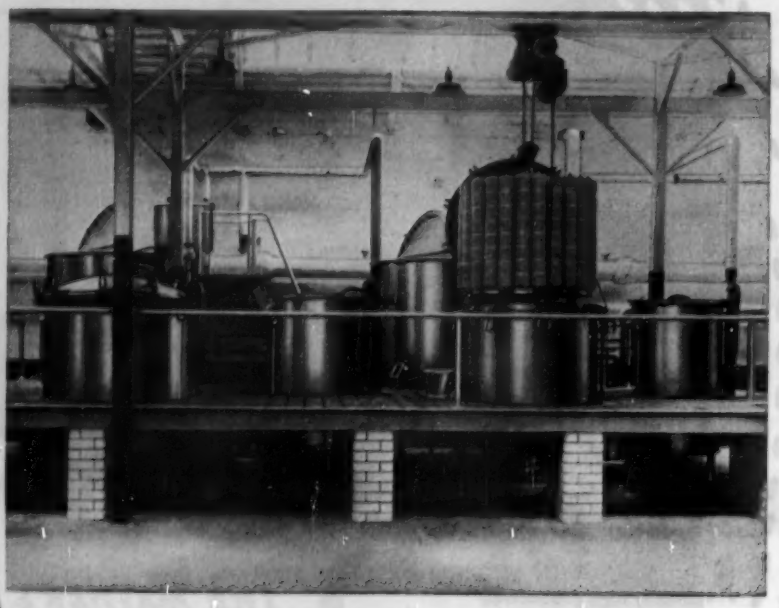

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NOTICE TO MEMBERS AND SUBSCRIBERS

Readers requiring *general information* regarding the Official Notices, List of Officers of the Society, etc. should consult pages 1–6 of the January 1954 and pages 229–232 of the July 1953 issues of the *Journal*, or write to *The Secretary*, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorkshire (*Telephone* Bradford 25138–9). *Editorial Communications* should be addressed to *The Editor*, at the same address.

Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

LECTURES

The Use of Organic Colouring Matters in Plastics
C. R. M. Oehlcke

COMMUNICATIONS

The Polarography of Azo Dyes *J. de O. Cabral and H. A. Turner*

The Combination of Wool with Acids *L. Peters and J. B. Speakman*

Analysis of Textile Auxiliary Products *J. A. van der Hoeve*

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FORTHCOMING MEETINGS OF THE SOCIETY

Thursday—8th April 1954 at 7-30 p.m.

ELEVENTH MERCER LECTURE N. W. Yelland, A.R.C.S., B.Sc., D.I.C. *Physics in the Dyeing, Printing, and Finishing Industries* Midland Hotel, Manchester 2

Friday—30th April 1954

ANNUAL GENERAL MEETING and DINNER of the Society Midland Hotel, Manchester 2

MIDLANDS SECTION

Except when stated otherwise, Lecture Meetings commence at 7.0 p.m.

1954	
Friday 26th March	MIDLANDS SECTION DINNER. King's Head Hotel, Loughborough
Wednesday 7th April	ANNUAL GENERAL MEETING OF SECTION. J. A. Potter, Esq., M.A. *Dyeing and Finishing Synthetic Fibres in the Hosiery Industry.* King's Head Hotel, Loughborough
Friday and Saturday 28th - 29th May	Exhibition *Scientific Aids to the Dyeing Industry.* College of Technology, Leicester (*Details later*)

MANCHESTER SECTION

Unless otherwise stated, meetings take place at the Textile Institute, 10 Blackfriars Street, Manchester 3, and commence at 6.30 p.m.

1954	
Friday 2nd April	ANNUAL GENERAL MEETING AND ADDRESS by the Chairman, G. S. J. White, Esq.

WEST RIDING SECTION

Meetings held at the Victoria Hotel, Bradford, at 7.15 p.m. unless otherwise stated

1954	
Thursday 25th March	LECTURE AND ANNUAL GENERAL MEETING
Tuesday 12th Jan.	S. Kershaw, Esq., F.T.I. (By invitation of the Yorkshire Section of the Textile Institute). *Experiences on a United Nations Assignment.* Midland Hotel, Bradford, at 7.15 p.m.
Monday 8th March	G. Kenneth Seddon, Esq. (By invitation of the Bradford Textile Society). *Interesting Points in Dyeing and Finishing.* Midland Hotel, Bradford, at 7.15 p.m.

NORTHERN IRELAND SECTION

All Meetings to be held in Royal Avenue Hotel, Belfast, at 7.30 p.m.

1954	
Late March or early April	ANNUAL GENERAL MEETING AND DINNER. (*Details later*)

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THE JOURNAL
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Volume 70 Number 3 MARCH 1954 Issued Monthly

Proceedings of the Society

Pressure Dyeing and Bleaching with special reference to Recent Developments

F. H. Marsh

Meeting of the Northern Ireland Section held at the Royal Avenue Hotel, Belfast, on 14th February 1953, Mr. D. A. Derrett-Smith in the chair

There are three main methods by which dyeing is performed—

(*a*) By moving the material to be dyed in a more or less static dyebath, e.g. piece or winch dyeing machines.

(*b*) By moving the material and the dyebath, the one medium moving faster than the other, e.g. paddle dyeing machines, both side paddle, i.e. oval paddle, and overhead paddle.

(*c*) By fixing or holding the material to be dyed firmly and moving the dye liquor. This type of dyeing is rapidly increasing and there are a wide variety of machines for operating in this way, e.g. the hank-dyeing machines, loose-material machines, top or slubbing dyeing units, and various types of package or pack dyeing units which dye cheeses, cones, rolls of narrow fabric, rayon cake, warp, or hank, etc., and loose-material machines where the material is made into a tight pack and the liquor forced through in a horizontal direction.

Where the material to be dyed is in a cheese or cone form the general term used is *package*.

Where packing in the material carrier is necessary the unit is generally called a *pack* and the machine a *pack-dyeing machine*.

The liquor may be circulated by either a propeller, pump, gravity, or by suction. There are various types of pumps such as centrifugal pumps, ram pumps, roots-type units, etc.

It would be correct to call all these machines described under (*c*) "pressure dyeing machines", but the generally accepted term today refers only to those machines where the material offers considerable resistance to flow, so that a pressure is set up which is easily measurable.

It will be appreciated that, where level dyeing can be obtained by movement of the dyebath only, the material being kept stationary, this is generally an ideal method of dyeing because the condition of the material remains generally the same after dyeing as when it enters the dyeing unit.

This statement is not true in every case, as sometimes advantage is taken of the dyeing process not only to dye the material but to change slightly the condition. For example, sometimes it is required to slightly "felt" woollen yarns to give them a lofty appearance.

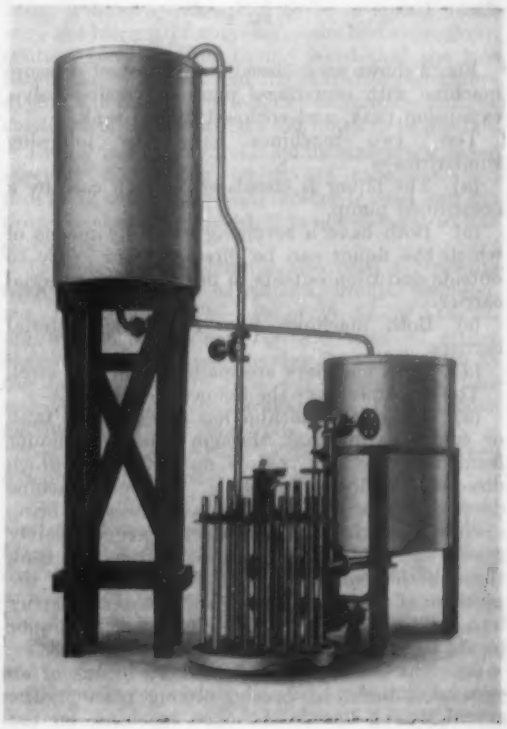

Fig. 1

Fig. 1 shows a typical stainless-steel open-type pressure dyeing machine with a cheese frame for dyeing packages up to 6 in. in diameter and with a reserve tank for preparing the liquor. The dye liquor is circulated by a centrifugal pump and the machine is fitted with a reversing valve for changing the direction of flow. Heating is performed by direct injection of steam into the dyeing tank.

The dye liquor prepared in the reserve tank can be transferred to the dyeing tank by gravity and can be pumped from the dyeing tank back to the reserve tank for recharging or storage by the circulating pump of the machine.

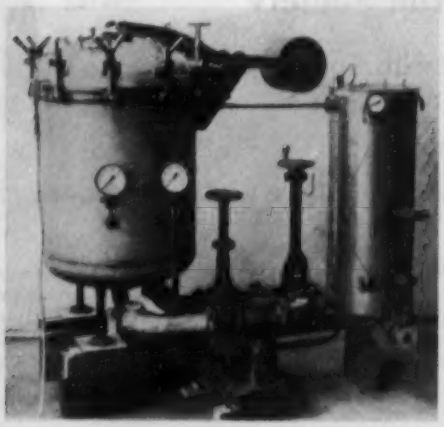

FIG. 2

Fig. 2 shows an enclosed stainless-steel pressure machine with centrifugal pump, reversing valve, expansion tank, and enclosed dyeing tank.

The two machines have the following similarities—

(*a*) The liquor is circulated in each case by a centrifugal pump.

(*b*) Both have a reversing valve by means of which the liquor can be directed from inside to outside and from outside to inside of the material carrier.

(*c*) Both machines take the same material carriers.

(*d*) Both machines are made of stainless steel.

The machines have the following differences—

(*a*) The closed machine has an expansion tank or compensating tank through which the liquor from the dye unit passes no matter in which direction the flow is travelling. The open machine does not require this extra tank, because being open to the atmosphere the tank is never completely filled, and the liquor is drawn from the tank through the pump and then forced back by the pressure of the pump through the material carrier into the tank again, so that the level of the liquor in the tank never varies.

(*b*) The closed unit is heated by means of an expansion tank, no heating taking place in the actual dyeing vessel; the open machine, on the other hand, is heated entirely by means of steam pipes in the dyeing vessel.

(*c*) The closed machine permits the flow in two directions, both under pressure; whilst the open machine allows pressure only in one direction, viz. when the liquor is travelling from inside to outside of the material carrier. This is a most important difference, and calls for further explanation.

When the liquor is travelling from the inside to outside of the package, the dyeing liquor in its most concentrated form first strikes the inside; as is passes through the package, it diverges and at the same time deposits dye, thus becoming less concentrated and therefore depositing progressively less dye. These two factors tend to produce a dyed package with a deeper shade from the inside to outside. Whether this is visible at the end of the dyeing will depend upon the type of dye, the ease with which the dye levels up, the depth of dyeing, etc.

When the flow is from outside to inside, however, the concentrated dye strikes first the outside of the package, tending to dye that part of the package more deeply than the inside, but this is counteracted by the fact that the liquor is converging towards the centre, and consequently there is more liquor per unit area.

It is obvious, therefore, that it is better to dye from outside to inside than from inside to outside.

On the open machine when dyeing from outside to inside, the flow is effected only by the suction of the pump, which is very much less than when the flow is obtained by pressure of the pump. The closed machine, therefore, offers a big advantage because dyeing can be carried out in both directions under pressure, particularly from outside to inside; consequently on enclosed machines most of the dyeing is done from outside to inside.

This point is far more important when dyeing packages than when pack dyeing, because the area ratio of inside to outside is very much greater on a cheese than on a pack cage.

The advantage of the closed machine does not apply when bleaching either linen or cotton in package form or when boiling off linen yarn, because the process is a slow one. For example, when bleaching, as long as the bleaching liquor in actual contact with the thread is replaced periodically, bleaching continues progressively and uniformly. The open-type pressure machine is therefore used quite successfully, and the closed machine, which is more costly offers no advantages.

The pressure machine is versatile and can be used for a wide variety of materials. It is used for dyeing cheeses and cones on the same material carrier, dyeing conical packages, the yarn may be wound directly on to a perforated centre, usually made of stainless steel, sometimes the yarn is wound on to a paper insert and transferred on to the perforated centre prior to dyeing. This procedure is not possible with wool and with medium to fine counts of cotton on account of the collapse of the package when the centre is removed.

After dyeing and extraction, the metal centre is more frequently replaced by a paper insert for drying and subsequent rewinding or warping. This procedure is effected to reduce the number of

stainless-steel perforated cones in circulation, on account of cost.

Cheeses can be dyed on compressible wire springs slipped over the stainless-steel perforated tubes, or the yarn first wound on wooden bobbins and transferred on to the dyeing tubes without any intermediate fittings. After dyeing it is put back on to bobbins having a flange at one end to prevent the packages slipping off the end of the bobbins. This latter method is more economical because the wooden tubes are cheaper, but slightly more labour is involved in the loading and unloading of the material carriers.

Whether the spring system or the wooden tube system is adopted depends entirely on local conditions; it is not possible to say that either system is superior to the other, no matter what are the particular conditions.

By inserting the pack-dyeing cage, the pressure machine can be used for dyeing either warps, hanks, or loose material. The material to be dyed is packed between two concentric perforated cylinders forming the cage. The width of the race, i.e. the packing space between the outer and inner cylinders, is determined by the material being dyed. When dyeing loose material the race is very much wider, the bulky nature of the material taking up much more packing space than yarn. Fig. 3 shows two cages, the top cage having a wide race for loose material, the bottom cage a narrow race for yarn.

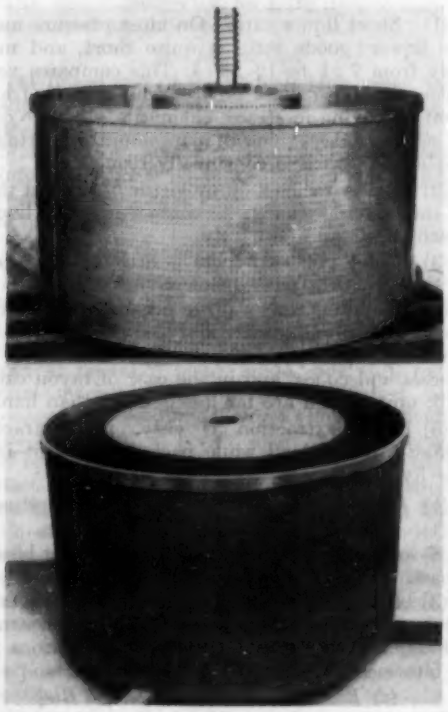

FIG. 3

The pressure machine is used widely for dyeing rayon cakes, the cakes are packed or better placed on plastic cake holders, the correct size to suit the particular size of cakes being dyed. The cakes are loaded on to columns on a material carrier or frame.

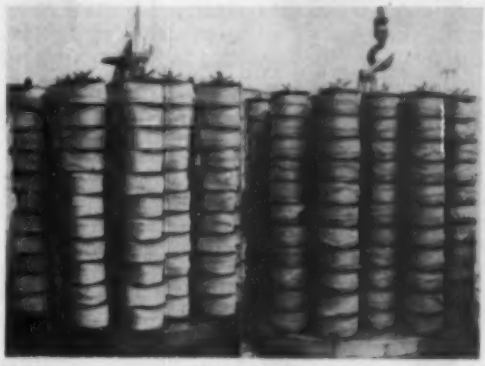

FIG. 4

Fig. 4 shows a frame of cakes before and after dyeing. It is essential that the correct size of cake holder is used and that the cakes are as near as practicable the same weight.

It is, however, much easier to dye cakes to-day than when cake dyeing was first introduced some sixteen years ago. At that time rayon cake dyeing being unknown, cakes had to be accepted which were not intended for dyeing; some had swansdown centres, some were so tightly laced that the lace bands had to be cut and the cakes relaced before dyeing, the variation in weight was immense and the condition of the actual cake left much to be desired.

To-day the major rayon spinners produce cakes specially for dyeing which are excellent, and providing the correct cake holder is used and the proper technique adopted, it is not difficult to dye successfully.

The pressure machine is also used for dyeing narrow fabrics such as ribbons, braids, webbing, etc., in roll form. The rolls of 36, 72, or 144 yd. are wound on to a perforated tube of either stainless-steel or plastic, having the same width as the fabric, and the rolls are slipped over the stainless-steel tubes forming the frame, thus making columns of such rolls.

One of the specialised applications of pressure dyeing is the treatment of beams.

For this form of dyeing a modified machine is used, built essentially on the same principle but fitted with a different type of pump and with a dyeing tank made to suit the beam, that is, small in diameter but comparatively great in depth. Fig. 5 shows a typical beam-dyeing machine.

There is a fundamental difference between beam and cheese dyeing; the former consists in dyeing a single package, tightly wound, with very little traverse, having a wall thickness of 6 in. or more of yarn; in the second case there are probably between 150 and 200 small packages comparatively

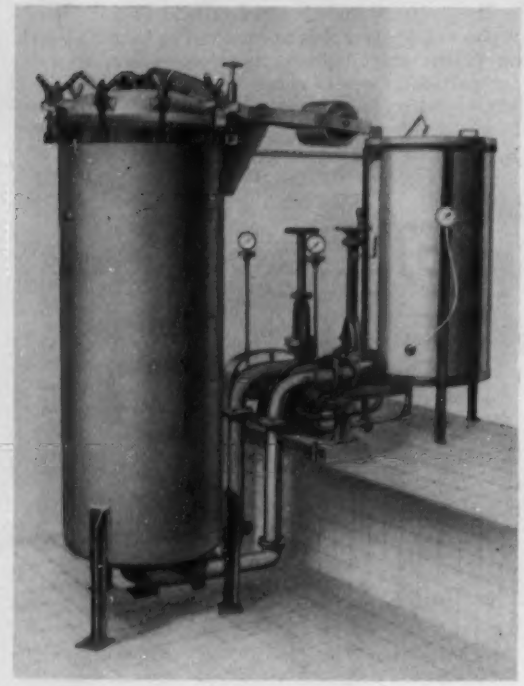

FIG. 5

softly wound with a great deal of traverse and having a wall thickness of, perhaps, 2½ or 3½ in. at the most.

Consequently for ideal dyeing of both types of packages a different type of pump is required, and this is why it is recommended that the processing of beams be done on a different machine and not on a combined cheese or beam machine.

In a manner similar to that used for cheeses the open pressure machine is used for bleaching, also for preboiling, and often for aftertreatment of beams.

Where production is such, therefore, that a number of dyeing units are needed, it is recommended the beams and small packages such as cheeses and cones be dyed on separate machines.

In the case of smaller dyehouses where the production does not justify several dyeing units, a combined beam and cheese machine is used; in this case the pump is modified to compromise between the ideal of both types of dyeing, and the densities of the beams and packages are adjusted as far as possible to suit.

MATERIAL USED FOR FABRICATION

Cast iron has been used to some extent where the liquors were alkaline or neutral in character, also mild steel, to a lesser extent, but these materials have obvious limitations and are unsuitable for bleaching.

Silicon cast irons have been tried on occasions.

For dyeing in acid liquors the early pressure machines were made with wooden tanks and gun metal or phosphor bronze pumps, these were suitable for only low pressure.

Copper has also been used and also Monel metal and Inconel, a non-ferrous alloy having a very high nickel content.

Stainless-steel-clad sheets have been tried; the basis of these consists of two sheets of metal, one stainless steel and the other mild steel, which are rolled and bonded together, the object being to obtain a sheet having an increased thickness and therefore able to withstand the pressure and yet containing only a thin sheet of stainless steel and therefore more economical.

The disadvantage of this type of material is that great care is needed to avoid contamination at the welds and thus to avoid the slightest trace of steel penetrating the stainless-steel, while, of course, the outside of the sheet rusts in the dyehouse atmosphere and the labour in manufacture is perhaps even greater than when fabricating entirely from stainless steel.

Machines made entirely of stainless-steel are by far the most popular and outnumber all other types.

There is, in fact, no other material for all-round general-purpose use anything like as good as stainless-steel, and while in recent years some attempts have been made to use synthetic materials either in solid form or as coatings or linings over steel, they all leave much to be desired.

ADVANTAGES AND DISADVANTAGES OF PRESSURE DYEING

The advantages of pressure dyeing are numerous and of considerable magnitude—

(*a*) *Cost of Process*

(1) Short liquor ratio. On most pressure units the liquor : goods ratio is quite short, and may vary from 7 : 1 to 12–14 : 1. This compares very favourably with most other forms of dyeing and means a saving in steam, chemicals, etc., the cost of steam to-day being of paramount importance and a cost which is continually rising.

(2) Better exhaustion by virtue of the fact that all the material comes into contact with the liquor continuously and positively.

(3) Being enclosed there is little or no escape of steam with a consequent saving.

(4) Handling time is down because the material carriers are lifted quickly and also the operative is handling 1–3-lb. packages at a time in the case of cheeses and cones, and in the case of rayon cakes 1-lb. units which are far less delicate than hanks.

(5) Hydroextraction is easy, the extractor taking a heavy load while pack cages to fit into the hydroextractor are available.

(*b*) *Better Working Conditions for the Operative*

(1) Mechanical handling.

(2) Absence of steam in the dyehouse or bleach house.

(3) More healthy conditions and less danger of injury to workers than in the steam-laden atmosphere, when an operative might walk into a pit or into moving parts of the plant, or carts.

(*c*) *Reduction of Human Element Risk*

It can be claimed that pressure dyeing and bleaching plant reduces the risk of danger due to

the human element. For example, modern machines are fitted with reserve tank facilities where complete baths of the liquor can be prepared, thus ensuring before dyeing complete solution of the dye; thermometers are fitted on most machines, mechanical means of flow reversal or stopping the flow can be fitted, all tending to reduce the human element risk.

(*d*) *Speed of Production*

Dealing with beams, the yarn is beamed for processing, bleached, dyed, aftertreated where necessary, vacuum-extracted, and then the beams of different colours are grouped behind the sizing or slashing machine, sized, dried, and put on to a back beam in the correct design for weaving. Dyed cheeses or cones can be warped directly after treatment without rewinding, and from dyed cones high-speed warping may follow.

Rayon cake dyeing offers big advantages, because the yarn is received ready for dyeing and after dyeing can be rewound at three times the speed permissible when winding from dyed hanks.

(*e*) *Quality of the Finished Product*

The quality of the dyed product is of a very high standard, because there is no movement of the material during dyeing.

(*f*) *Stainless Steel*

Finally, the plant being of stainless-steel, it gives all the advantages that this material offers in the dyeing trade, such as cleanliness, brightness of shade in dyeing, quick change over from dark to light shades.

The disadvantages of pressure dyeing may be summarised as follows—

(*a*) *Initial Cost*

The initial cost of the plant is high, since, being made entirely of stainless-steel and having to withstand considerable pressure, it must be fabricated from heavy-gauge material and heavily reinforced. A well made and well designed plant, however, should have a long life and largely offset the initial cost.

(*b*) *Greater Care in Control*

More care is needed in controlling the machine and therefore a high grade of labour is necessary to operate the plant. Mistakes in operating can be very costly and there is more danger of certain types of mistakes being made, not only to the actual machine but the textile product being processed. For example if a dye which is difficult to dissolve is used in heavy shade, when dyeing in the open beck, if not properly dissolved at the outset sinks to the bottom and slowly dissolves with the agitation of the steam. The long liquor ratio also helps and the material— suspended on sticks above the bottom never comes into direct contact with undissolved dye, thus quite possibly the result will be satisfactory. If, however, the dyeing had been in package form the dye would at once have been filtered on to the material and the possibility of a satisfactory dyeing would be remote

At first sight this statement that greater care in control is necessary may seem at variance with the earlier statement that a modern dyeing plant reduces the risk due to the human element, but the machine maker is continually facing two complicated problems, namely designing a plant to cut out manual operation and to make the process of dyeing more foolproof, and yet on the other hand this makes the plant more complex, which calls for a higher grade of labour to be responsible for the maintenance. This is the hall-mark of evolution and cannot be stopped.

(*c*) *Lack of Visibility*

The lack of visibility of the material being processed may be a disadvantage to some dyers who have been in the habit of always watching the material being dyed, but as more enclosed machines replace open types and the operative gets increasing skill and knowledge this will largely disappear.

(*d*) *More Maintenance*

Machines tending to become more complex call for a higher degree of maintenance.

METHODS OF HEATING

Electricity is a very clean and efficient way of heating a machine and on laboratory machines is used regularly, but in the British Isles the price of electricity prohibits its use for commercial machines.

Where there is an abundant supply of water power, which makes for cheap electricity, then it can be and is used; even here, however, it is more economical to use an electrically heated flash boiler and so first produce steam and then heat the actual liquor by use of this steam.

The main methods in general use for heating pressure machines are open steam pipes, closed coils, and high-pressure hot water.

Open steam pipes are initially the cheapest to instal but not necessarily the cheapest to use.

Closed coils are more expensive, because a comparatively large surface area of pipe is needed to raise the temperature of the liquor in a reasonable time.

The closed coil, however, has the advantage that there is no contamination of the materials by dirt from the steam, either because the boilers prime, or on a Monday morning or after a holiday, due to scale and rust from the pipes, this can be a great source of trouble and can cause the dyer a good deal of anxiety and worry.

High-pressure hot-water heating is now being used more frequently. In this system the water is heated under pressure until it attains a temperature of 170–180°C., and it is then pumped around the system and eventually returns to the boilers at 130–100°C., the higher the temperature of the return the better because this system is based on high-speed flow, so that the surface of the coil is always at a very much higher temperature than the surrounding medium. This system can only pay when used in a big installation, that is where the dyehouse forms only a part of the plant. It is exceedingly costly to install, but once installed is a most efficient system.

With high-pressure hot water and closed steam coils there is no dilution of the dyebath by condensation, this may be a very big saving because it is often necessary to have the full quantity of dye liquor to commence circulation and, if therefore the starting temperature is very low, considerable dilution will take place before boiling point is reached.

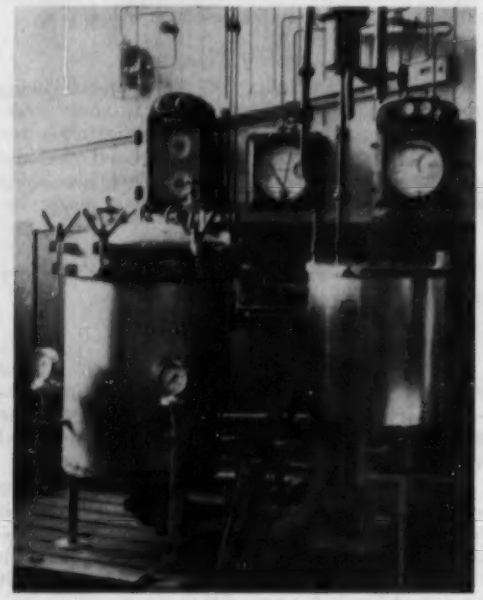

FIG. 6

AUTOMATIC CONTROLS

Automatic controls can be of considerable use. Fig. 6 shows a 30-lb. capacity totally enclosed pressure machine fitted with—

(*a*) Process timer for reversing the direction of flow automatically at predetermined periods.

(*b*) A thermostatic temperature control.

(*c*) A time-temperature controller.

A single machine would not be fitted with both (*b*) and (*c*), but the illustration is used to show the types of controller available.

Combined dyeing and hydroextractor cages are sometimes used in high-speed production plants; in this case the warp, hank, or loose-material cage from the dyeing machine is designed to fit into a special type of hydroextractor, the cage must be so constructed as to withstand the centrifugal force imposed during the extraction and must be dynamically balanced to ensure smooth running.

SPECIAL-PURPOSE PRESSURE-DYEING MACHINES

Apart from the standard types of pressure-dyeing machines previously described, there are special-purpose machines designed for doing one particular type of work. For example, there is a demand in the carpet trade for a single piece of plain carpet dyed to a particular shade to match surroundings in an existing room. To dye sufficient yarn to make up one or two pieces, say 60 yd. × 27 in. wide, is very costly, there is a wastage because the amount of yarn to be dyed must be far in excess of what is actually needed, while considerable time is taken to produce the carpet from the date of order, consequently for this type of special order the carpet can be dyed after actual manufacture from grey yarn. Fig. 7 shows a roll of carpet prepared for dyeing on a pressure machine designed specially for this work.

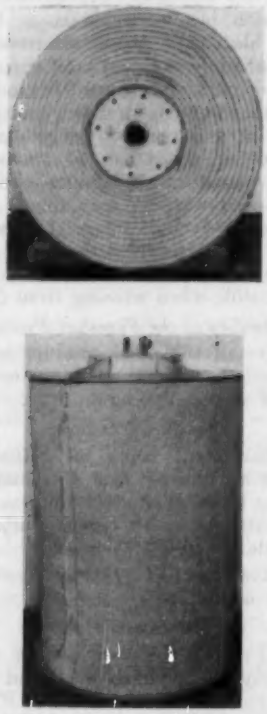

FIG. 7

FELT DYEING ON BEAMS

Rolls of felt are dyed in special-purpose pressure-dyeing machines, and Fig. 8 shows a machine designed for this work.

The felt is rolled on to the perforated beam, which is fitted with a movable top flange in the form of a header which can be screwed down on to the selvage of the rolled felt and so make a joint preventing escape of the dye liquor. Distance pieces can be inserted to allow for varying widths of felt to be processed on the same beam.

RECENT DEVELOPMENTS

Since the end of the second world war synthetic fibres have begun to play an ever more prominent part in textiles. Nylon is widely used, while Ardil and Terylene are being used in increasing quantity. All these fibres have their own specific dyeing problems and Terylene has proved a particularly difficult fibre to dye satisfactorily, especially in medium and deep shades. The disperse or acetate-rayon range of dyes can be applied at normal temperatures, i.e. up to 100°C. only in pale and some medium shades.

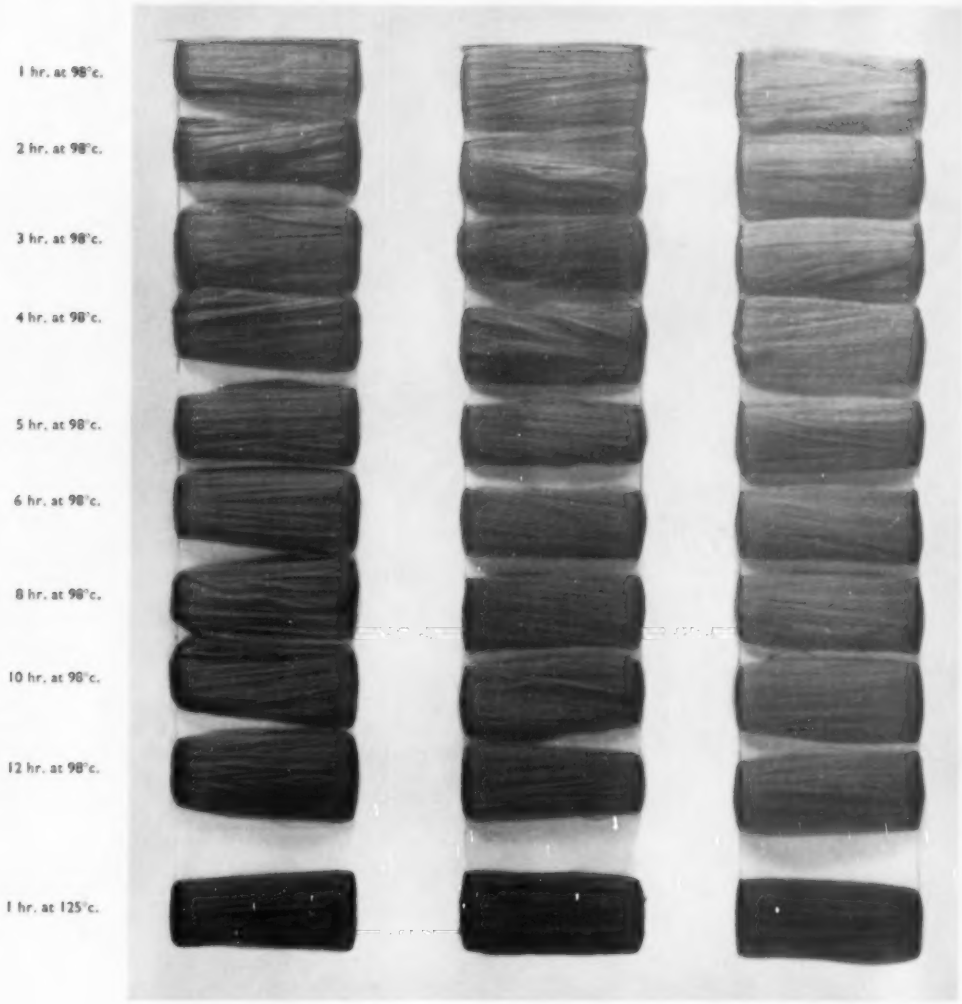

FIG. 9—7% Dispersol Fast Scarlet B 150

FIG. 10—6% Duranol Blue G 200 Paste

FIG. 11—6% Duranol Brilliant Violet B 300

FIG. 9–11—Dyeings on 140-denier Terylene

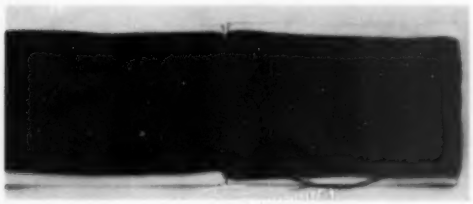

FIG. 12—7% Dispersol Fast Scarlet B 150 dyed for 1 hr. at 125°c.

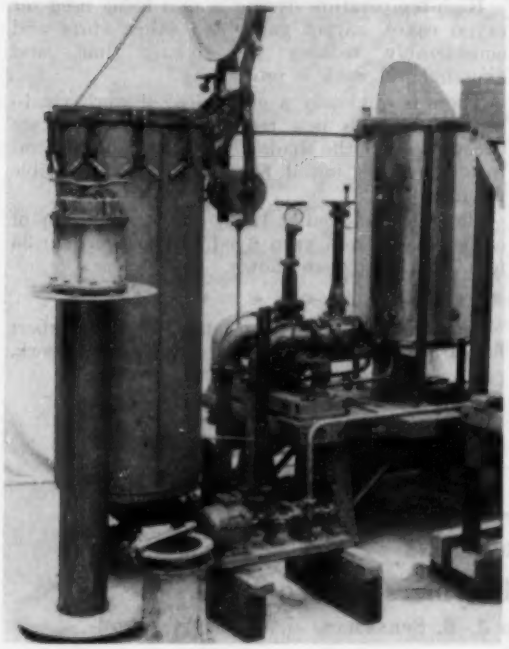

FIG. 8

Carriers or swelling agents can be used to increase the affinity of the dyes for the fibre, and Waters [1] has dealt fully with the variety of such agents, but according to Turnbull [2] the ideal carrier should be odourless, non-volatile, non-inflammable, non-toxic, water-soluble, effective in low concentration, have a low cost, and be easily removable after dyeing. Carriers so far available fall a long way short of the ideal carrier.

It has been shown that the speed of exhaustion increases rapidly with increase in temperature above 100°C., and full shades, dark browns, navy blues, and blacks can be rapidly obtained in the normal dyeing time without damage to the fibre.

Fig. 9–11 show the depth of shade obtained on 140-denier Terylene when dyed for 1–12 hr. at 98°C., and also the same yarn dyed under identical conditions except that the temperature was 125°C. dyeing for 1 hr. only.

The samples are wrappings taken from cheeses dyed with—

7% Dispersol Fast Scarlet B 150	...	Fig. 9
6% Duranol Blue G 200 paste	...	Fig. 10
6% Duranol Brilliant Violet B 300	...	Fig. 11

It will be seen that after 12 hr. dyeing at 98°C. the depth of shade in each case is less than obtained in 1 hr. at 125°C., the latter giving a full shade.

Trials carried out with Dispersol Fast Scarlet B 150 showed that 12 hr. dyeing time at 98°C. followed by 1 hr. dyeing time at 125°C. gave no increased depth of shade over dyeing obtained in 1 hr. at 125°C.

During the dyeing of disperse dyes some filtration of the aggregate particles occurs; this is very pronounced at temperatures below 100°C., but at high temperatures the particles are taken partly into solution and dyeing proceeds.

Even at 125°C., however, some filtration of dye persists, and at the end of the dyeing must be removed to avoid marking off and lack of rubbing fastness.

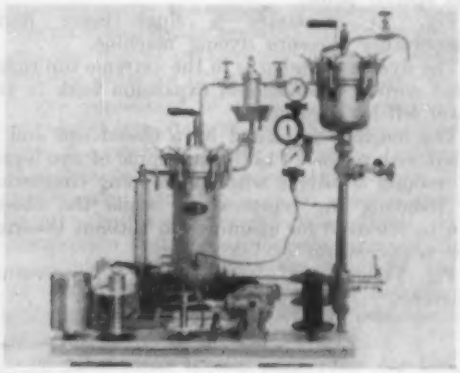

FIG. 13

A method of doing this, consisting in destroying the solid dye by reduction, has been suggested.[3] The package is treated for 15 min. at 75°C. in a bath containing per litre, 2 g. caustic flakes, 2 g. sodium hydrosulphite, and 2 g. Lissolamine A 50 paste. After this "reduction clear" process, the material is rinsed in a cold bath containing, per litre, 0·5 g. caustic soda and 0·5 g. sodium hydrosulphite, and then rinsed again in cold water.

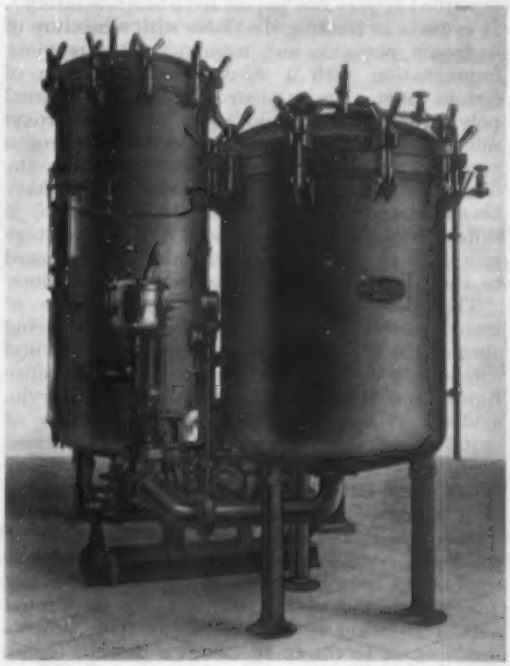

FIG. 14

This process completely destroys all the loose colour without affecting the depth of shade, the Terylene acting as resist and so preventing any breakdown of the actual dyed molecules within the fibre. Fig. 12 indicates that there is no loss in depth of shade by this treatment.

Dyeing at 125°C. demands a special technique and special plant.

Fig. 13 illustrates a single-cheese high-temperature pressure dyeing machine.

The dyeing chamber is in the extreme top right-hand corner, the enclosed expansion tank in the lower left-hand corner.

The machine is heated by a closed coil and is fitted with means of taking a sample of dye liquor or making additions without stopping circulation or reducing the temperature, while the cheese can be removed for examination without lowering the temperature.

Fig. 14 shows a commercial high-temperature machine.

High-temperature dyeing is also being used for rayon cakes, carpet yarn, and other fibres and considerably reduces the dyeing time, and experimental work is proceeding.

There is obviously a great deal of work yet to be done on this new technique, many dyes are decomposed or the shade altered at high temperatures, but the initial results show considerable promise.

Rayon cakes dyed at 120°C. and a sample slip of carpet made from yarn dyed and matched in 35 min. at 110°C. were shown.

* * *

The author wishes to thank Mr. K. Limbert for carrying out much of the experimental work.

(*MS received 31st March 1953*)

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[1] Waters, J.S.D.C., **66**, 609 (1950).
[2] Turnbull, *Amer. Dyestuff Rep.*, **41**, 75 (1952).
[3] Douglas, G. T. Private communication.

COMMUNICATIONS

The Formation of Polymers in Wool

G. W. MADARAS AND J. B. SPEAKMAN

When potassium persulphate is used in place of hydrogen peroxide, it is unnecessary to impregnate wool with ferrous ammonium sulphate in order to ensure preferential polymerisation of methacrylic acid inside the fibres at 25°C. Polymerisation is initiated by the free radicals which are formed by the action of potassium persulphate on the cystine disulphide bonds. With reduced fibres, however, potassium persulphate is not much more effective than hydrogen peroxide.

An "anchored catalyst" technique for synthesising vinyl polymers inside wool fibres has been described in previous papers from this laboratory [1]. It consists in treating the fibres with a mixture of hydrogen peroxide and monomer after previous impregnation with a dilute, acidic solution of ferrous ammonium sulphate. Preferential internal polymerisation is brought about by the hydroxyl radicals which are formed when the hydrogen peroxide reacts with the ferrous ions within the fibres. Although highly successful results have been obtained by means of this technique, it suffers from the disadvantage of being a two-stage process, and attention has therefore been turned to the development of a more simple procedure.

The Fe^{++}–peroxide system is only one of many possible mixtures of oxidising and reducing agents which initiate the polymerisation of vinyl compounds by free radical formation [2], and since Lipson and Hope [3] have shown that methacrylic acid undergoes polymerisation in the presence of cysteine and ammonium persulphate, it seemed likely that wool containing cysteine side-chains would itself initiate polymerisation on immersion in a mixture of oxidising agent and monomer. There is a remote possibility that the trace of combined cysteine normally present in untreated wool might be sufficient to cause polymerisation, but, if not, the wool would have to be treated with a reducing agent, and a two-stage process would again be the result. Such a process, unlike the Fe^{++}–peroxide process, would suffer from the further disadvantage that the "anchored catalyst" is obtained by damaging the fibres. There remains the possibility that intact disulphide bonds may give rise to free radicals in reaction with some oxidising agents, though this does not seem to be the case with hydrogen peroxide. In that event, internal polymerisation would be promoted by the wool itself on treatment with a solution containing an oxidising agent and monomer.

With the preceding considerations in mind, the behaviour of untreated and chemically modified wools in reaction with solutions containing methacrylic acid and an oxidising agent has been examined.

Experimental

PREPARATION OF MATERIALS

(*a*) FLANNEL — An all-wool flannel weighing 5·5 oz./sq.yd. was used throughout the investigation. For most of the experiments, patterns 5 in. square, weighing about 3·0 g., were cut from the flannel and purified by extraction with alcohol and ether in a Soxhlet apparatus, followed by washing in six changes of distilled water at 50°C. To remove traces of iron from the wool, it was immersed in a large volume of dilute hydrochloric acid (pH 2) for 48 hr. at room temperature and then washed in several changes of distilled water until the pH of the solution in equilibrium with the wool rose to 4·5. The patterns were then removed, centrifuged, conditioned at 65% R.H. and 22·2°C., and weighed. Samples of the purified flannel, both before and after treatment with

hydrochloric acid, were ignited, and the ash was tested for iron with thioglycollic acid. Whereas the ash from the wool which had not been treated with hydrochloric acid gave a purple coloration, that from the acid-treated wool did not.

(*b*) METHACRYLIC ACID — Copper-stabilised methacrylic acid was kindly provided by Imperial Chemical Industries Ltd. The inhibitor was removed and the monomer purified by fractional distillation under reduced pressure in an atmosphere of nitrogen. The fraction boiling at 78–80°C. under a pressure of 12 mm. of mercury was collected and kept in a refrigerator, no sample being used after more than one week's storage. Its purity, as determined by the bromine absorption method of Kaufmann and Hartweg [4], was found to be 98%.

(*c*) CYSTINE AND CYSTEINE HYDROCHLORIDE — The B.D.H. products were analysed, with the following results —

L-CYSTINE —
Found — N 11·70; S 26·59.
Theory — N 11·66; S 26·69.

L-CYSTEINE HYDROCHLORIDE —
Found — N 8·55; S 20·05; Cl 22·50.
Theory — N 8·89; S 20·35; Cl 22·50.

METHODS

(*a*) REDUCTION — The 0·1 N. solution of potassium thioglycollate (pH 4·45–4·50) which was normally used was prepared by adding 9 c.c. (approx.) of thioglycollic acid (B.D.H.) to 120 c.c. (approx.) of 1·0 N. potassium hydroxide and making up to 1 litre, the exact concentration of thioglycollic acid in the solution being determined by titration with iodine. Each pattern of flannel was wetted out with distilled water under reduced pressure, squeezed, and then treated with 100 c.c. of the solution of potassium thioglycollate for 15–18 hr. at 35–40°C., the exact time and temperature being known in each experiment. Except where otherwise stated, the pattern was afterwards washed in running water for 18 hr.

(*b*) METHYLATION — Each pattern was wetted out, squeezed, and then treated with 150 c.c. of an ethereal solution of diazomethane [5] (0·15–0·16 M.) for 48 hr. at room temperature in the dark. The treatment was repeated, and the pattern then washed in six changes of alcohol, followed by several changes of distilled water.

(*c*) ETHYLATION — After the pattern had been wetted out with a 0·2 M. phosphate buffer solution (pH 8·0), it was squeezed and immersed in 85 c.c. of the buffer solution, to which 0·5 c.c. of ethyl bromide had been added (0·002 mole of ethyl bromide per gram of wool), for 20 hr. at 35°C. The sample was then washed well with 0·05 M. buffer, 0·01 M. buffer, and distilled water in succession.

(*d*) POLYMERISATION — After pretreatment, if necessary, the pattern was introduced into a 100 c.c. Pyrex flask, which was immersed in a thermostat at 25 ± 0·05°C. and connected to a vacuum line and a supply of oxygen-free nitrogen. Distilled water (40 c.c.) was then added, and the pressure reduced to 12 mm. of mercury for 10 min. before admitting nitrogen, which was allowed to stream slowly through the flask. At this stage, methacrylic acid (2·5 c.c.) and the appropriate amount of either hydrogen peroxide or potassium persulphate were dissolved in distilled water (10 c.c.), and the solution, after being freed from dissolved oxygen by a stream of oxygen-free nitrogen, was added to the flask. At the end of the reaction period, the amount of unreacted monomer was estimated by the bromine-absorption method [4], and the flannel pattern was removed, washed in running water for 12 hr., conditioned, and weighed.

The percentage of monomer polymerised was calculated from its initial and final concentrations, with a correction for the amount of methacrylic acid removed from the solution (initial pH 2·3) by combination with the wool in cases where little or no polymer was formed in the fibres. On the assumption that the acidic polymer would have a much higher affinity than the monomer, no such correction was applied when the deposition of polymer was large in relation to the acid-combining capacity.

In subsequent tables, each value for the gain in weight of the flannel is expressed as a percentage of the original weight of the conditioned, untreated pattern. When patterns containing large amounts of polymer were extracted with alcohol (90% by wt.) for 16 hr. in a Soxhlet apparatus, there was only a slight loss in weight (0·4%), indicating that the polymer was deposited inside the fibres, as was suggested by the appearance and feel of the fabric.

RESULTS

(*a*) *Formation of Polymer in Untreated and Chemically Modified Wools with Potassium Persulphate as the Oxidising Agent*

REDUCTION — 100 c.c. of 0·1 N. potassium thioglycollate for 15 hr. at 35°C.

METHYLATION — As described.

POLYMERISATION — 1 hr. at 25°C. with 0·1 g. potassium persulphate.

TABLE I

State of Wool	Oxidising Agent	Increase in Weight (%)	Amount of Monomer Polymerised (%)
Wool absent	$K_2S_2O_8$	—	4·4
Untreated	None	0·6	2·5
Untreated	$K_2S_2O_8$	36·1	45·4
Untreated — methylated	None	− 0·1	9·2
Untreated — methylated	$K_2S_2O_8$	44·4	62·8
Reduced	None	0·6	6·0
Reduced	$K_2S_2O_8$	29·4	61·4
Reduced — methylated	None	− 0·9	10·7
Reduced — methylated	$K_2S_2O_8$	45·8	68·2

(*b*) *Comparison of Potassium Persulphate and Hydrogen Peroxide as Oxidising Agents with Untreated and Reduced Wools*

REDUCTION — 100 c.c. of 0·1 N. potassium thioglycollate for 18 hr. at 35°C.

METHYLATION AND ETHYLATION — As described.

POLYMERISATION — 1 hr. at 25°C. with 0·1 g. potassium persulphate or 1 c.c. of 0·2 vol. hydrogen peroxide. It will be noted that the amounts of oxidising agent are not equivalent; the results obtained with equimolar quantities are given in Table VII.

TABLE II

State of Wool	Oxidising Agent	Increase in Weight (%)	Amount of Monomer Polymerised (%)
Untreated	$K_2S_2O_8$	42·6	54·8
Untreated	H_2O_2	4·5	18·1
Untreated — methylated	$K_2S_2O_8$	44·8	61·3
Untreated — methylated	H_2O_2	7·8	38·2
Untreated — ethylated	$K_2S_2O_8$	42·4	51·3
Untreated — ethylated	H_2O_2	4·3	16·3
Reduced...	$K_2S_2O_8$	29·0	61·4
Reduced...	H_2O_2	27·0	68·8
Reduced — methylated	$K_2S_2O_8$	41·7	66·3
Reduced — methylated	H_2O_2	9·9	55·8
Reduced — ethylated ...	$K_2S_2O_8$	36·3	54·6
Reduced — ethylated ...	H_2O_2	13·7	44·5

(c) *Comparison of Potassium Persulphate and Hydrogen Peroxide as Oxidising Agents with Wools reduced to Different Extents*

REDUCTION — 100 c.c. of 0·1, 0·2, or 0·4 N. potassium thioglycollate for 16 hr. at 40°C. *Washed with distilled water.*

POLYMERISATION — 1 hr. at 25°C. with 0·1 g. potassium persulphate or 1 c.c. of 0·2-vol. hydrogen peroxide.

TABLE III

State of Wool	Oxidising Agent	Increase in Weight (%)	Amount of Monomer Polymerised (%)
Untreated...	$K_2S_2O_8$	41·6	46·8
Untreated...	H_2O_2	6·5	28·5
Reduced — 0·1N. thioglycollate	$K_2S_2O_8$	30·8	65·3
Reduced — 0·1N. thioglycollate	H_2O_2	14·5	39·3
Reduced — 0·2N. thioglycollate	$K_2S_2O_8$	35·4	62·0
Reduced — 0·2N. thioglycollate	H_2O_2	17·9	43·6
Reduced — 0·4N. thioglycollate	$K_2S_2O_8$	37·2	73·3
Reduced — 0·4N. thioglycollate	H_2O_2	21·6	52·0

(d) *Effect of Previous Oxidation of the Wool on the Formation of Polymer*

OXIDATION— *Hydrogen peroxide*— 100 c.c. of either 2-vol. or 20-vol. hydrogen peroxide for 12 hr. at 40°C.

Potassium persulphate— 100 c.c. of either 0·1 M. or 0·2 M. potassium persulphate for 12 hr. at 40°C.

Peracetic acid— 100 c.c. of 0·2 M. peracetic acid for 12 hr. at 40°C.

After oxidation, the patterns were washed with several changes of distilled water.

POLYMERISATION— 1 hr. at 25°C. with 0·1 g. potassium persulphate.

TABLE IV

Oxidising Agent	Increase in Weight (%)	Amount of Monomer Polymerised (%)
None	41·6	46·8
2-vol. Hydrogen peroxide ...	34·9	57·2
20-vol. Hydrogen peroxide ...	33·1	43·3
0·1 M. Potassium persulphate	3·6	5·1
0·2 M. Potassium persulphate	3·3	6·9
0·2 M. Peracetic acid	— 5·5	8·6

(e) *Effect of Cystine and Cysteine in promoting the Polymerisation of Methacrylic Acid in presence of Potassium Persulphate or Hydrogen Peroxide*

As cystine is sparingly soluble in distilled water, cystine and cysteine hydrochloride were both dissolved in 0·1 N. hydrochloric acid for use in promoting the polymerisation of methacrylic acid in presence of either hydrogen peroxide or potassium persulphate. Similar experiments were carried out with cysteine hydrochloride dissolved in distilled water. Each solution contained 50 c.c. of distilled water or 0·1 N. hydrochloric acid, 2·5 c.c. of methacrylic acid, 0·15 g. of amino acid, and either 0·1 g. of potassium persulphate or 1 c.c. of 0·2-vol. hydrogen peroxide. Polymerisation was allowed to proceed for 2 hr. at 25°C., and the results are given in Table V.

TABLE V

Reaction Medium	Amino Acid	Oxidising Agent	Polymerisation (%) in 1 hr.	2 hr.
0·1 N. HCl	L-Cystine	$K_2S_2O_8$	12·9	29·3
	L-Cystine	H_2O_2	6·7	17·0
	L-Cysteine HCl	$K_2S_2O_8$	30·2	48·0
	L-Cysteine HCl	H_2O_2	33·9	53·7
Distilled Water	L-Cysteine HCl	$K_2S_2O_8$	81·5	88·0
	L-Cysteine HCl	H_2O_2	57·0	72·1

As there is a possibility that the preceding results may be affected by the liberation of chlorine atoms by the action of the oxidising agent on the hydrochloric acid, the experiments were repeated with cystine and cysteine hydrochloride dissolved in 0·2 N. sulphuric acid. In this case, equimolecular concentrations of cystine and cysteine hydrochloride, as well as of potassium persulphate and hydrogen peroxide, were used. Each solution contained 50 c.c. of distilled water or 0·2 N.

TABLE VI

Reaction Medium	Amino Acid	Oxidising Agent	Polymerisation (%) in 1 hr.	2 hr.
0·2 N-H_2SO_4	L-Cystine	—	Nil	Nil
	None	$K_2S_2O_8$	4·6	14·0
	L-Cystine	$K_2S_2O_8$	9·3	22·3
	None	H_2O_2	Nil	Nil
	L-Cystine	H_2O_2	0·8	2·3
	L-Cysteine HCl	—	0·1	0·7
	L-Cysteine HCl	$K_2S_2O_8$	20·0	33·9
	L-Cysteine HCl	H_2O_2	17·8	30·6
Distilled water	L-Cysteine HCl	—	0·4	1·1
	None	$K_2S_2O_8$	6·2	16·2
	L-Cysteine HCl	$K_2S_2O_8$	78·3	92·1
	None	H_2O_2	Nil	Nil
	L-Cysteine HCl	H_2O_2	75·9	91·2

sulphuric acid, 2·5 c.c. of methacrylic acid, 0·15 g. cystine or 0·098 g. cysteine hydrochloride, and either 0·027 g. potassium persulphate or 1·0 c.c. of 1·12-vol. hydrogen peroxide. Polymerisation was allowed to proceed for 2 hr. at 25°C., and the results are given in Table VI.

(g) Comparison of Untreated Wool, Reduced Wool, Cystine, and Cysteine as Promoters of the Polymerisation of Methacrylic Acid in presence of Potassium Persulphate or Hydrogen Peroxide

In these experiments, 1·5-g. patterns of flannel were used, so that the cystine content would be similar to the amount of cystine used in corresponding experiments with the free amino acid. Each reduced pattern was prepared by 18 hours' treatment at 35°C. with 100 c.c. of 0·2 N. potassium thioglycollate (pH 4·45), followed by washing in running water for 18 hr. In polymerisation experiments, each pattern was treated with a mixture of 50 c.c. of 0·2 N. sulphuric acid or distilled water, 2·5 c.c. methacrylic acid, and either 0·027 g. potassium persulphate or 1·0 c.c. of 1·12-vol. hydrogen peroxide, for 1 hr. at 25°C. The pattern was then washed in running water for 12 hr., conditioned, and weighed.

In the experiments with amino acids, polymerisation was allowed to proceed for 1 hr. at 25°C., the concentrations of the reagents being exactly the same as in the preceding experiment. Hydrochloric acid, in an amount equivalent to that present in the cysteine hydrochloride, was added to the reaction mixture when cystine was used, so that strictly comparable results would be obtained with the two amino acids.

TABLE VII

Medium	Sulphur Compound	Oxidising Agent	Increase in Weight (%)	Amount of Monomer Polymerised (%)
0·2 N-H_2SO_4	Untreated wool	$K_2S_2O_8$	49·4	54·0
		H_2O_2	11·5	21·7
	Reduced wool	$K_2S_2O_8$	41·1	71·6
		H_2O_2	28·2	74·5
	L-Cystine	$K_2S_2O_8$	—	11·6
		H_2O_2	—	2·3
	L-Cysteine HCl	$K_2S_2O_8$	—	18·5
		H_2O_2	—	17·8
Distilled water	Untreated wool	$K_2S_2O_8$	35·1	29·4
		H_2O_2	9·1	14·8
	Reduced wool	$K_2S_2O_8$	33·5	64·4
		H_2O_2	31·6	70·9
	L-Cysteine HCl	$K_2S_2O_8$	—	79·2
		H_2O_2	—	75·9

Discussion

From the results of Table I it is evident that neither untreated wool, nor methylated wool, nor potassium persulphate will separately promote the polymerisation of methacrylic acid in 1 hr. at 25°C. When, however, untreated or methylated wool is used in conjunction with potassium persulphate, large amounts of polymer are formed in the fibres. Similarly, there is little polymerisation when reduced wool or reduced-and-methylated wool is treated with methacrylic acid, but considerable polymerisation takes place in presence of potassium persulphate, especially in the case of reduced-and-methylated wool.

With hydrogen peroxide, on the other hand, far more polymer is formed in reduced wool than in untreated wool, as shown in Table II, and it seems likely that the cysteine side-chains are responsible for the difference, because little polymer is formed if the reduced wool is ethylated or, better still, methylated before use in polymerisation experiments. Further, the extent to which polymer is deposited increases with increasing degree of reduction of the wool (Table III), though the corresponding results with potassium persulphate as the oxidising agent suggest that this effect may be complicated, not only by the increasing swelling and accessibility of the fibres, but also by the dual function of the thiol groups. Besides promoting the decomposition of the persulphate ion, as shown below, they serve as chain transfer agents by reacting with the growing polymer chains ($P_m^{\cdot}$)—

$$P_m^{\cdot} + R\text{–}SH \rightarrow P_mH + RS^{\cdot}$$

This results in the synthesis of shorter polymer chains, some of which may be removed during subsequent washing of the wool.

Although the results of Table II seem to indicate that potassium persulphate is always better than hydrogen peroxide in promoting polymerisation, especially in the case of untreated wool and reduced-and-methylated wool, the comparison is unfair because equimolar concentrations of oxidising agent were not used. Similar results were, however, obtained with equimolar concentrations in aqueous and acidic media, as shown in Table VII, and there can be no doubt that potassium persulphate is far more effective than hydrogen peroxide in promoting the formation of polymers in untreated wool.

When cystine is used instead of wool to promote the polymerisation of methacrylic acid, the same difference between potassium persulphate and hydrogen peroxide is again observed (Tables V–VII), the former being very much more effective. It seems probable, therefore, that the action of wool and potassium persulphate in promoting the polymerisation of methacrylic acid is associated with the action of potassium persulphate on the cystine bonds of wool. Support for this view is to be found in the fact that wool previously treated with potassium persulphate does not promote the formation of polymer during subsequent treatment with a mixture of methacrylic acid and potassium persulphate (Table IV). Polymerisation is, however, obtained with wool which has been previously treated with hydrogen peroxide, as would be expected from the fact that hydrogen peroxide is so much less effective than potassium persulphate in promoting the formation of polymer in wool.

The preferential internal polymerisation of methacrylic acid is, presumably, due to the formation of free radicals by the action of either hydrogen peroxide or potassium persulphate on the thiol groups of reduced wool, and, in the case of untreated wool, by the action of potassium

persulphate on the disulphide cross-links. Possible reaction schemes are as follows—

REDUCED WOOL

$$R\text{–}SH \rightleftharpoons R\text{–}S^- + H^+$$

$$(a)\ R\text{–}S^- + S_2O_8^{2-} \rightarrow {}^{\bullet}SO_4^- + SO_4^{2-} + R\text{–}S^{\bullet}$$

$${}^{\bullet}SO_4^- + H_2O \rightarrow HSO_4^- + {}^{\bullet}OH$$

$$\text{or } (b)\ R\text{–}S^- + H_2O_2 \rightarrow R\text{–}S^{\bullet} + OH^- + {}^{\bullet}OH$$

Polymerisation is brought about by the free radicals as follows—

$$R\text{–}S^{\bullet} + CH_2{=}\underset{\underset{COOH}{|}}{C}(CH_3) + CH_2{=}\underset{\underset{COOH}{|}}{C}(CH_3) + \text{etc} \rightarrow$$

$$R\text{–}S\text{–}CH_2\text{–}\underset{\underset{COOH}{|}}{C}(CH_3)\text{–}CH_2\text{–}\underset{\underset{COOH}{|}}{C}(CH_3)\text{–}$$

and similarly with the ${}^{\bullet}SO_4^-$ and ${}^{\bullet}OH$ radicals.

It seems probable that ionisation of the thiol group is rate-determining in the above mechanism, because, as shown in Tables V–VII, cysteine is much less successful in promoting polymerisation in an acid medium than in distilled water.

UNTREATED WOOL

$$R\text{–}S\text{–}S\text{–}R \rightleftarrows 2\ R\text{–}S^{\bullet}$$

$$R\text{–}S^{\bullet} + S_2O_8^{2-} \rightarrow R\text{–}S\text{–}O\text{–}SO_3^- + {}^{\bullet}SO_4^-$$

$$R\text{–}S\text{–}O\text{–}SO_3^- \rightarrow R\text{–}S^{\bullet} + {}^{\bullet}SO_4^-$$

$${}^{\bullet}SO_4^- + H_2O \rightarrow HSO_4^- + {}^{\bullet}OH$$

As in the case of reduced wool, polymerisation is initiated by the free radicals.

The above mechanism involves splitting of the O–O bond of the persulphate ion, which requires an activation energy of 33·5 kg.cal./mole [9], and it is significant, in connection with the greater effectiveness of potassium persulphate, that the bond-dissociation energy of hydrogen peroxide is greater. According to Bolland and Gee [7], the value is not greater than 66 kg.cal./mole, and Evans, Hush, and Uri [8] have obtained a calculated value of 46·7 kg.cal./mole. Even more significant, in view of the greater effectiveness of potassium persulphate in acid solution (Table VII), is the fact that the activation energy for the acid-catalysed decomposition of the persulphate ion is only 26·0 kg.cal./mole [9].

* * *

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The Design and Construction of a Differential Refractometer for Measurements on Coloured Solutions

E. ATHERTON and E. COWGILL

A differential refractometer, suitable for the measurement of refractive indices of dyes, is described, and some of its uses are indicated. The instrument is of the prism type, utilising a small spectrometer to provide monochromatic light. Refractive index values are obtained by means of a rotating mirror driven by a differential screw, which cancels the deviation conferred on the light beam by the dye solution.

Several advantages of the instrument for measurements in spectral regions of maximum absorption are discussed.

INTRODUCTION

Few studies of the refractive indices of dyes have been reported in the literature. The first accurate measurements were carried out by Pflüger and his co-workers [1], on Fuchsin and Rosaniline, by measuring the displacement of a light beam after passing through a prism of solid dye with a small refracting angle. Their results were later checked and confirmed by Walter [2] and Wood [3] by measurements of Brewsterian angle. The relationships obtained between refractive index and wavelength exhibited the expected anomalous dispersion for an absorbing molecule, as predicted by classical theory.

Since then, little interest has been shown in measuring refractive indices. This is surprising, because knowledge of the polarisability of a molecule is valuable in understanding its physical and chemical properties. In addition, the refractive index of a substance and its dispersion with wavelength would be expected to influence the optical properties of a medium in which the substance is incorporated. This is clearly illustrated by the hiding power of a paint film, which depends to a large extent on the difference in refractive index between the pigment and the medium. There is not such an important dependence of the optical properties of a dyed fabric on the refractive index of the dye, but some optical effects are to be expected in spectral regions between absorption bands of the dye, where the reflectance is governed by the Fresnel coefficient of the dyed fibres and hence by their refractive indices.

Anomalous effects have in fact been noted by Nutting [4], whose curves of reflectance against wavelength for dyed wool patterns showed an anomalous increase in the red and orange regions of the spectrum, which may well be interpreted

in terms of the increased refractive index of the fibre due to the presence of dye [5].

In addition to being valuable in the study of this phenomenon, knowledge of the refractive indices of dye solutions must be obtained as part of any quantitative study of aggregation by light scattering [5–7].

The instrument to be described was constructed for these purposes. It is simple to use, and with a little experience a complete refractive index–wavelength curve of a dye solution in the visible spectrum may be obtained in less than 30 min.

DESIGN OF THE INSTRUMENT

Many types of differential refractometer have been constructed for measurements with colourless solutions. The highest degree of precision and reliability yet obtained (excluding interferometric methods) is achieved by instruments of the type described by P. P. Debye [8]. In his instrument a collimated beam of light was passed through a hollow glass prism containing a solution, which was situated inside a cubical glass cell filled with solvent. The light beam suffered a small angular displacement due to the refractive index difference between the two liquids and, in leaving the outer cell, was further refracted at the glass–air interface. It was focussed on to a filar eyepiece so that displacements of the slit image could be measured directly. The displacement caused by replacing the solution in the prism with solvent was determined, and after calibration with known solutions the refractive index of the solution under investigation could be calculated. By this method refractive index differences of the order 10^{-5}–10^{-6} could be measured. In carrying out measurements to this degree of precision, accurate thermostating of the cells was necessary, but, since the solution was completely surrounded by solvent, temperature equilibrium was rapidly established. In this respect differential refractometers have marked advantages over interferometers, since in the latter solution and solvent are physically separated, and temperature equilibrium is established only slowly.

Instruments of the type described are not, however, suitable for measurements with strongly absorbing solutions, since the light beam fills the full aperture of the prism, causing considerable reduction of intensity. Nonetheless, the differential principle is suitable for this type of measurement, since it depends upon an interfacial effect rather than upon a finite path length in solution (as does an interferometer). The inherent difficulty in using the Debye type of instrument may be overcome by concentrating the incident light into a narrow beam and passing it through the solution near the refracting angle of the prism. The deflection sensitivity is maintained and the short path length in solution reduces absorption to a minimum. The following simple analysis relates angular deviation to refractive index difference.

The cell assembly is shown in Fig. 1, in which α is the total angular deviation and D is the angular deviation caused by the prism.

Since D is very small, minimum deviation may be assumed, and hence—

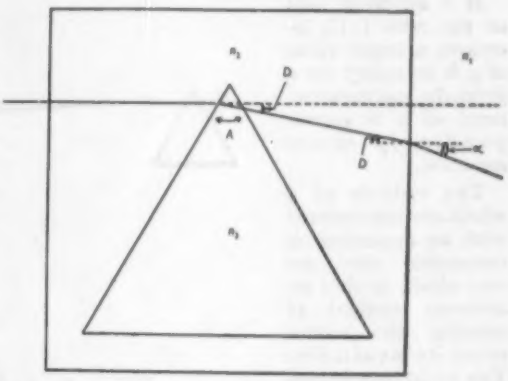

FIG. 1

$$\frac{n_2}{n_3} = \frac{\sin (A + D)/2}{\sin A/2} \qquad \text{(i)}$$

also

$$n_2 \sin D = n_1 \sin \alpha$$

Thus

$$\sin \alpha = (n_2/n_1) \sin D$$

or, since the angles are small—

$$\alpha = (n_2/n_1)\, D \qquad \text{(ii)}$$

If A is 60°, equation (i) becomes—

$$\sin [(60 + D)/2] = \tfrac{1}{2}\,(n_2/n_3)$$

or $$D = 2 \sin^{-1} (\tfrac{1}{2}\, n_2/n_3) - \pi/3 \text{ in radians}$$

Substitution for D in equation (ii) gives—

$$\alpha = n_2/n_1 \{2 \sin^{-1} (\tfrac{1}{2}\, n_2/n_3) - \pi/3\}$$

Now $n_3 = n_2 + \Delta n$ (where Δn is the refractive index increase due to the solute), hence—

$$\alpha = n_2/n_1 \left\{ 2 \sin^{-1} \tfrac{1}{2} \left(\frac{n_2 + \Delta n}{n_2} \right) - \pi/3 \right\}$$

that is, total angular deviation =

$$n_2/n_1 \left\{ 2 \sin^{-1} \left(0{\cdot}5 + \frac{\Delta n}{2n_2} \right) - \pi/3 \right\} \qquad \text{(iii)}$$

In general, this angular deviation has been measured in previous instruments as the linear displacement of a slit image, but it may be directly measured with advantage. This may be done by interposing a mirror between the cells and the eyepiece, and adjusting the slit image to a fixed index mark for each solution studied by a small rotation of the mirror. This arrangement is shown in Fig. 2, in which M is the mirror and A–A' the focal plane of the eyepiece. If the path length from the prism to the mirror is l_1 and from the mirror to the focal plane is l_2, the lateral movement of the image in the focal plane is $(l_1 + l_2)\, \alpha$.

If an angular rotation φ of the mirror brings the image back to the cross-wires in the eyepiece, then the linear displacement of the image is—

$$2 \varphi l_2 = (l_1 + l_2)\, \alpha$$

or $$\varphi = \left(\frac{l_1 + l_2}{2l_2} \right) \alpha \qquad \text{(iv)}$$

The angular rotation of the mirror which is required, when the refractive index of the solution changes by Δn, is—

$$\varphi = \left(\frac{l_1 + l_2}{2l_2} \right) n_2/n_1 \left\{ 2 \sin^{-1} \left(0{\cdot}5 + \frac{\Delta n}{2n_2} \right) - \pi/3 \right\} \text{(v)}$$

It is apparent that as the ratio $l_1 : l_2$ increases, a larger value of φ is necessary for a given Δn, and measurement of φ is correspondingly more accurate.

The values of φ which are encountered with an apparatus of reasonable size are very small, so that an accurate method of rotating the mirror must be available. This could be achieved by connecting a long rigid arm to the mirror and noting the angular rotation of the arm in terms of the displacement of the end. This method would be extremely clumsy, and equally good results may be obtained with a differential screw which bears upon a short arm connected to the mirror. The principle of a differential screw is shown in Fig. 3.

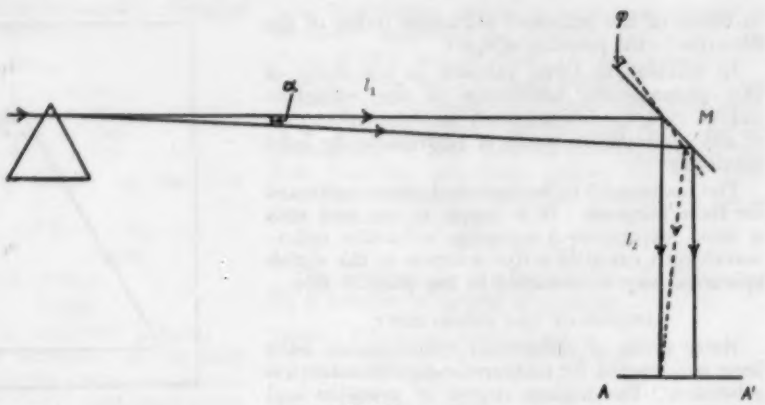

FIG. 2

On a screwed rod X on which is located a cylindrical nut ZZ' (length 2 in.), carrying a gear wheel which meshes with the barrel gear G. The other end of the nut, which is also threaded carries another screwed rod Y, which is prevented from rotation by a key in the bush B which engages in a keyway in the rod. The screw threads on the rod have 40 and 45 threads per inch respectively. The end of Y bears against a hardened steel insert in an arm A connected rigidly to a rod at right angles to the plane of the diagram. The screw assembly is spring loaded by a tension spring S. Rotation of the barrel gear causes the nut to unscrew from X and to screw on to Y. The resulting linear movement of Y for one rotation of the nut is $\left(\frac{1}{40} - \frac{1}{45} = \frac{1}{360}\right)$ in. and this causes A to rotate by an angle—

$$\varepsilon = \frac{1}{a \times 360} \text{ radians}$$

where a is the length of A.

The differential screw incorporated in the instrument has an angular reduction factor of approximately 2×10^3, which, as will be seen later, is adequate for the contemplated uses of the instrument.

The layout of the instrument is shown in Fig. 4. Light from a 36-watt auto bulb is rendered monochromatic by a small Hilger constant-deviation spectrometer and is focussed by lenses in the focal plane of an eyepiece. The monochromatic light beam, 2 mm. in width, passes through a hollow glass cube containing solvent (water) in which is cemented a hollow glass prism with 60° angles, containing solution. It is then reflected back by a front-aluminised mirror and deviated through a right angle by a second mirror mounted on the output shaft of a differential screw. The input shaft carries a pointer which indicates its angular setting on a circular scale divided into 100 equal intervals. All the components are screwed to a 1 in. thick base of seasoned wood. No greater dimensional stability is required than can be attained with this arrangement, since the apparatus is always calibrated with standard sucrose solutions before use.

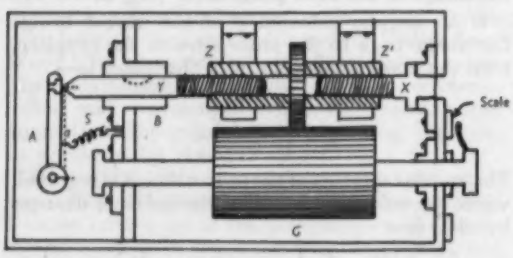

FIG. 3—Differential Screw
(Scale of Drawing 1 : 2)

With the construction described, one revolution of the differential screw input shaft causes the mirror to rotate through $3{\cdot}183 \times 10^{-3}$ radians.

The values of l_1 and l_2 are 132·5 and 5·0 cm. respectively, so that—

$$\frac{l_1 + l_2}{2l_2} = 27{\cdot}5$$

From equation (v) therefore, the calibration equation of the instrument is—

$$\theta = \frac{27{\cdot}5}{3{\cdot}183} \times 10^3 \times 1{\cdot}333 \left\{ \sin^{-1}\left(0{\cdot}5 + \frac{\Delta n}{1{\cdot}666}\right) - \pi/3 \right\} \text{(vi)}$$

where θ is the number of revolutions of the screw for an increment Δn, when the outer cell is filled with water at 20°c. ($n_{_{2\ 20}} = 1{\cdot}33300$).

In order to check the calibration equation, several sucrose solutions of known refractive index were prepared, and observations of the screw revolutions obtained. These were compared with the theoretical values obtained from the calibration equation (Table I).

TABLE I

Calibration of Refractometer

Concn. of Soln. (% by wt.)	n^D_{20}	Δn	Revolutions of Input Shaft	
			Calculated	Observed
0	1·33300	0	0	0
0·3	$1{\cdot}33342_4$	$4{\cdot}2 \times 10^{-4}$	2·010	2·00
0·7	$1{\cdot}33398_3$	$9{\cdot}8 \times 10^{-4}$	4·860	4·85
1·0	$1{\cdot}33440_4$	$14{\cdot}1 \times 10^{-4}$	7·038	7·04
1·3	$1{\cdot}33482_7$	$18{\cdot}3 \times 10^{-4}$	9·104	9·12

MEASUREMENTS WITH DYE SOLUTIONS

As examples of the use of the instrument measurements carried out on Edicol Supra Erythrosine AS (*C.I.* 773) and Naphthalene Fast Orange 2GS (*C.I.* 27) may be quoted. The curves of Δn against wavelength are shown in Fig. 5 and 6. The measurements were carried out at 21°C. and 23°C. respectively, the instrument being first calibrated with sucrose solutions. The curves show the characteristic anomalous dispersion of refractive index in the region of the absorption bands, and are similar in character to those found by Cooper for organic pigments by measurement of Brewsterian angle[9].

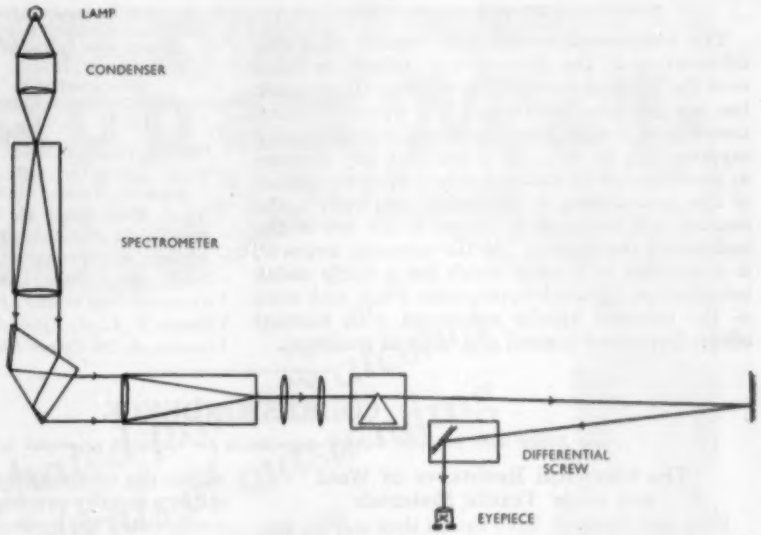

FIG. 4

Although the laws of mixture relating to refractive index of solutions are complex, an approximate value of the refractive index of the dye may be obtained by assuming a simple additive relationship to exist—

$$n_s = n_D f_D + n_W f_W \qquad \text{(vii)}$$

where n_s = Refractive index of the solution
n_D = Refractive index of the dye
n_W = Refractive index of the water
f_D = Weight fraction of dye
f_W = Weight fraction of water

Writing $f_W = (1 - f_D)$ and rearranging terms gives—

$$\frac{\Delta n}{f_D} = (n_D - n_W) \qquad \text{(viii)}$$

where Δn is the difference in refractive index between the solution and solvent.

At a wavelength of 5500 A. and assuming $n_W = 1{\cdot}3$, calculations of $\Delta n/f_D$ from the graphs give—

Edicol Supra Erythrosine AS

$$\frac{\Delta n}{f_D} = \frac{3 \times 10^{-4}}{2{\cdot}5 \times 10^{-4}} = 1{\cdot}2 \quad n_D = 2{\cdot}5$$

Naphthalene Fast Orange 2G

$$\frac{\Delta n}{f_D} = \frac{3{\cdot}74 \times 10^{-4}}{5 \times 10^{-4}} = 0{\cdot}75 \quad n_D = 2{\cdot}08$$

which are of the order found by Cooper for some organic pigments on the long-wavelength side of the absorption band.

A further point of interest is that in the region 4800–5100 A. the refractive index of water is reduced by the addition of dye in consequence of the anomalous dispersion. This corresponds in the instrument to negative mirror rotations, and the calibration curve may be extended to cover such cases by filling the prism with water and the outer cell with sucrose solution.

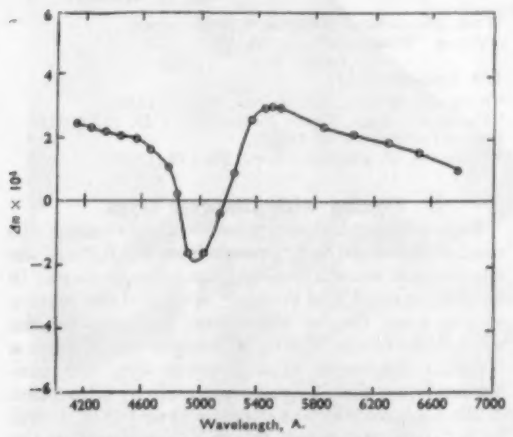

FIG. 5—Edicol Supra Erythrosine AS (0·25 g./litre at 21°C.)

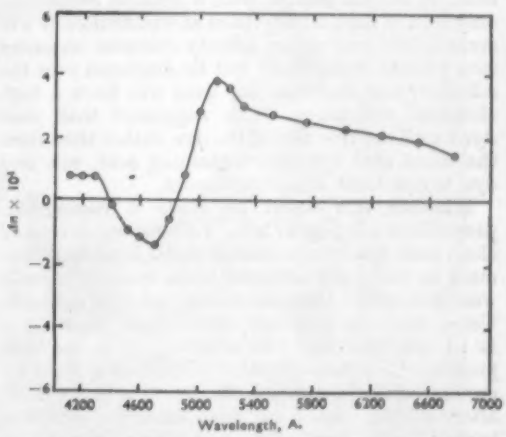

FIG. 6—Naphthalene Fast Orange 2GS (0·5 g./litre at 23°C.)

DISCUSSION OF THE INSTRUMENT

The instrument described is capable of giving information of the dispersion of refractive index over the whole of the visual spectrum. Its precision has not yet been determined but repeat measurements show a satisfactory degree of reproducibility (approx. 2% in Δn). It is felt that any increase in precision can be attained only if the temperature of the optical cells is controlled, and such modification will be made in future if the use of the instrument demands it. At the moment, however, it is situated in a room which has a fairly stable temperature (diurnal fluctuations 2°C.), and none of the troubles usually associated with thermal effects have been noticed (e.g. drift of readings).

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CORRESPONDENCE

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The Electrical Resistance of Wool and other Textile Materials

King and Medley [1] have shown that the conduction of electricity in keratin at moderate to high regains is ionic in character, i.e. the electricity is not carried by electrons as in a metal but by the ions of electrolytes present in the wool as impurities. Marsh and Earp [2] had previously shown that the conductivity of wool could be reduced by prolonged washing. The present author [3] has studied the behaviour of ions in horn keratin, in contact with electrolyte solutions and has shown, using radioactive tracers, by what proportion each ion species contributes to the conductivity. From this work it is possible to predict the magnitude of the conductivity of various types of ions in keratin. In particular, ions that have a high affinity for the keratin have very low mobilities, e.g. dye ions and hydrogen ions; whereas ions from simple electrolytes such as KCl, Na_2SO_4, etc. have much higher mobilities. Although this is for saturation regains, the effects will be similar for moderate to high regains[1].

The treatment of wool to give it a high electrical resistance is of commercial importance, as, for example, when it is to be used for electrical insulation. If wool is treated with a solution containing only ions of high affinity then at equilibrium it will contain few ions of low affinity (because impurity ions present in the wool will be displaced into the solution) and therefore the wool will have a high electrical resistance. It is suggested that wool dyed with the free acid of the dye, rather than from the usual acid dyebath containing acid, salt and dye would fulfil this requirement.

Whether this could be made a commercial proposition is open to test. Laboratory dyeing of clean loose wool has indicated that a 20 : 1 improvement in resistance occurred when free-acid dyeing was used rather than the traditional acid dyebath. Using wool as received after alkali scouring a 10 : 1 improvement was achieved by a one-bath process. In normal practice when dyeing wool for use in electrical insulation, the dyer has to wash-off, after dyeing, until he has removed sufficient loosely bound ions, such as sulphate ions, to be within the conductivity specification; this may be rather a lengthy process because of the low diffusion coefficient of the hydrogen ions [2]. If the wool, to be dyed with the free dye acid, is alkaline, it may be necessary to use excess dye acid to neutralise it or better, to use two successive baths. To give level dyeing, since no salt is to be present, the rate of dyeing would have to be controlled by temperature alone; also the exhaustion of the bath will not be good because there is no excess of mineral acid present. It is possible in many cases to obtain the free dye acids by "salting-out" commercial dyes using a mineral acid. Another method of conversion is by the use of ion-exchange resins [4].

Presumably similar ideas could be applied to the treatment of other textiles or paper when they are to be used for electrical insulation. (For papers, a less effective but similar procedure is being used when they are washed with magnesium sulphate; simple bivalent ions are known to have lower mobilities than univalent ones.) If it is not desired to colour the materials, it would be necessary to use uncoloured compounds of high affinity; for example in the case of wool the free acids of some proprietary mothproofing agents, which are usually applied by acid dyeing methods, would be suitable.

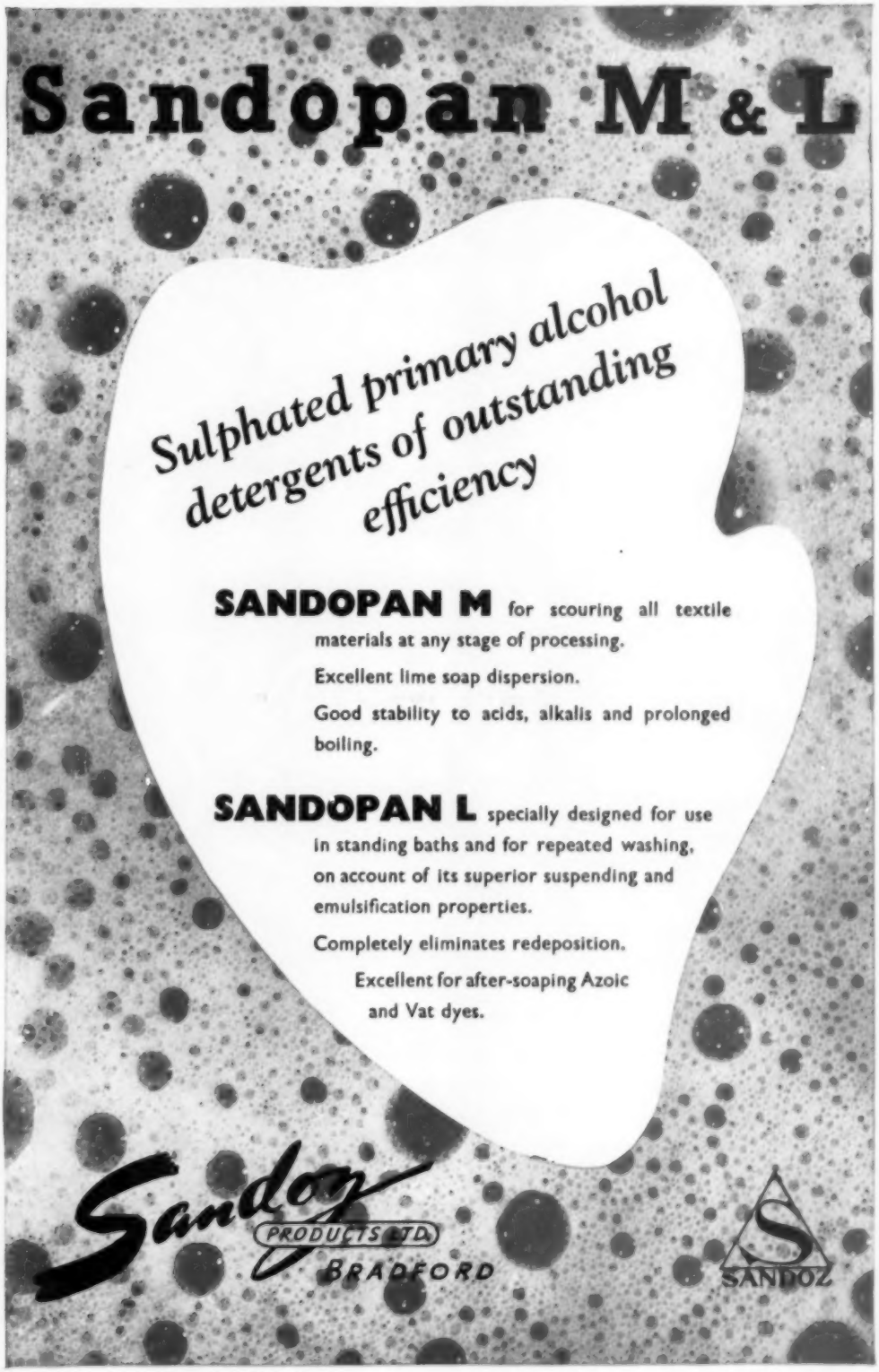
M. L. WRIGHT

WOOL INDUSTRIES RESEARCH ASSOCIATION
"TORRIDON"
LEEDS 6
11th November 1953

[1] King and Medley, *J. Coll. Sci.*, **4**, 1, 9 (1949).
[2] Marsh and Earp, *Trans. Faraday Soc.*, **29**, 173 (1933).
[3] Wright, *ibid.*, **49**, 95 (1953).
[4] Kressman, *J. Physical Chem.*, **56**, 118 (1952).

Dyeing with Disperse Dyes

It is usual to draw inferences concerning the mechanism of a dyeing process from the form of the equilibrium absorption isotherm. For example, in 1942 Vickerstaff and Waters [1] discussed the bearing of the form of the absorption isotherm on the mechanism of the dyeing of acetate rayon from a colloidal dispersion of a disperse dye, one conclusion being that if dyeing proceeds by adsorption of the Langmuir type a curve of type I (Fig. 1) will be obtained, whereas if the dye "dissolves" in the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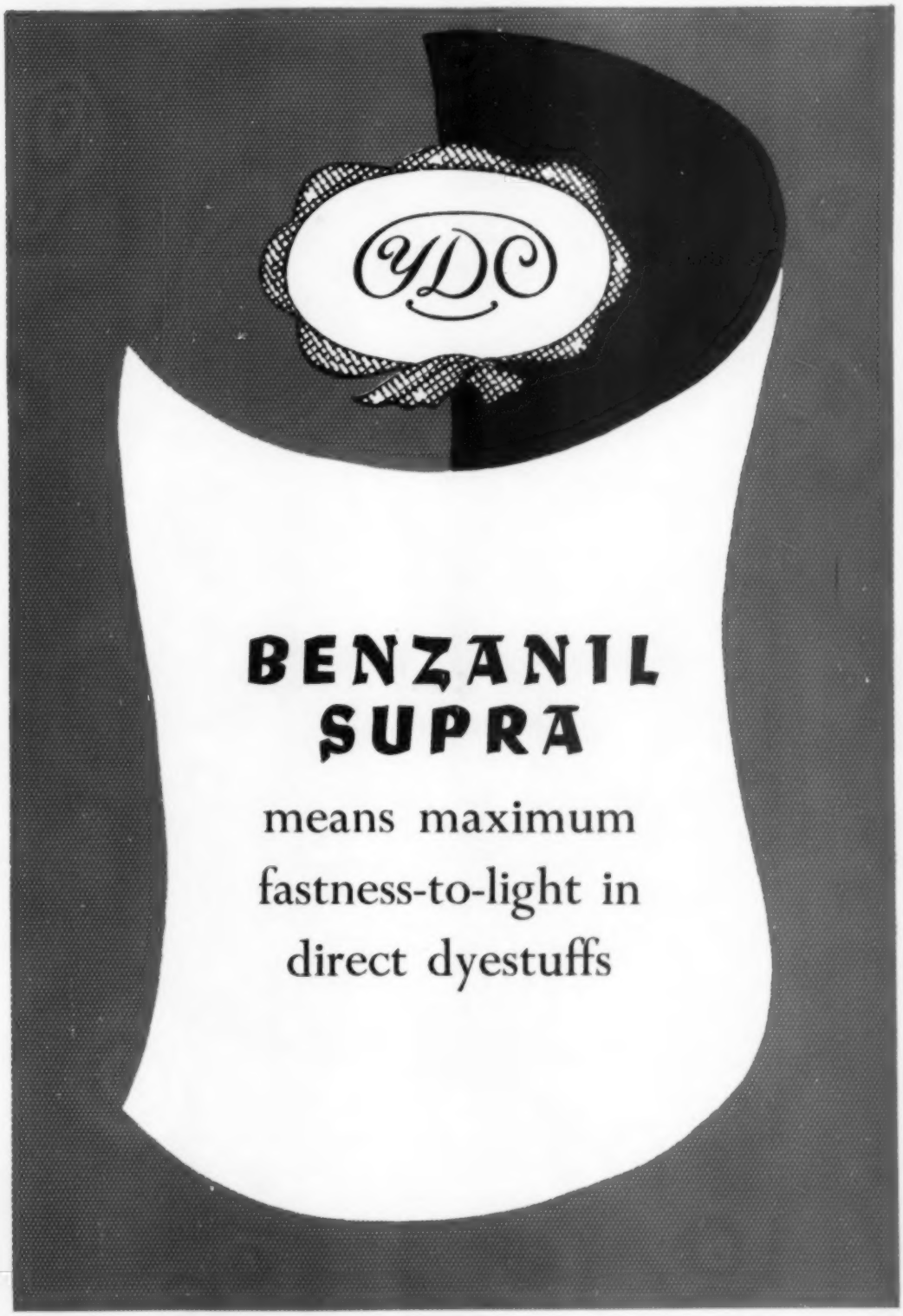

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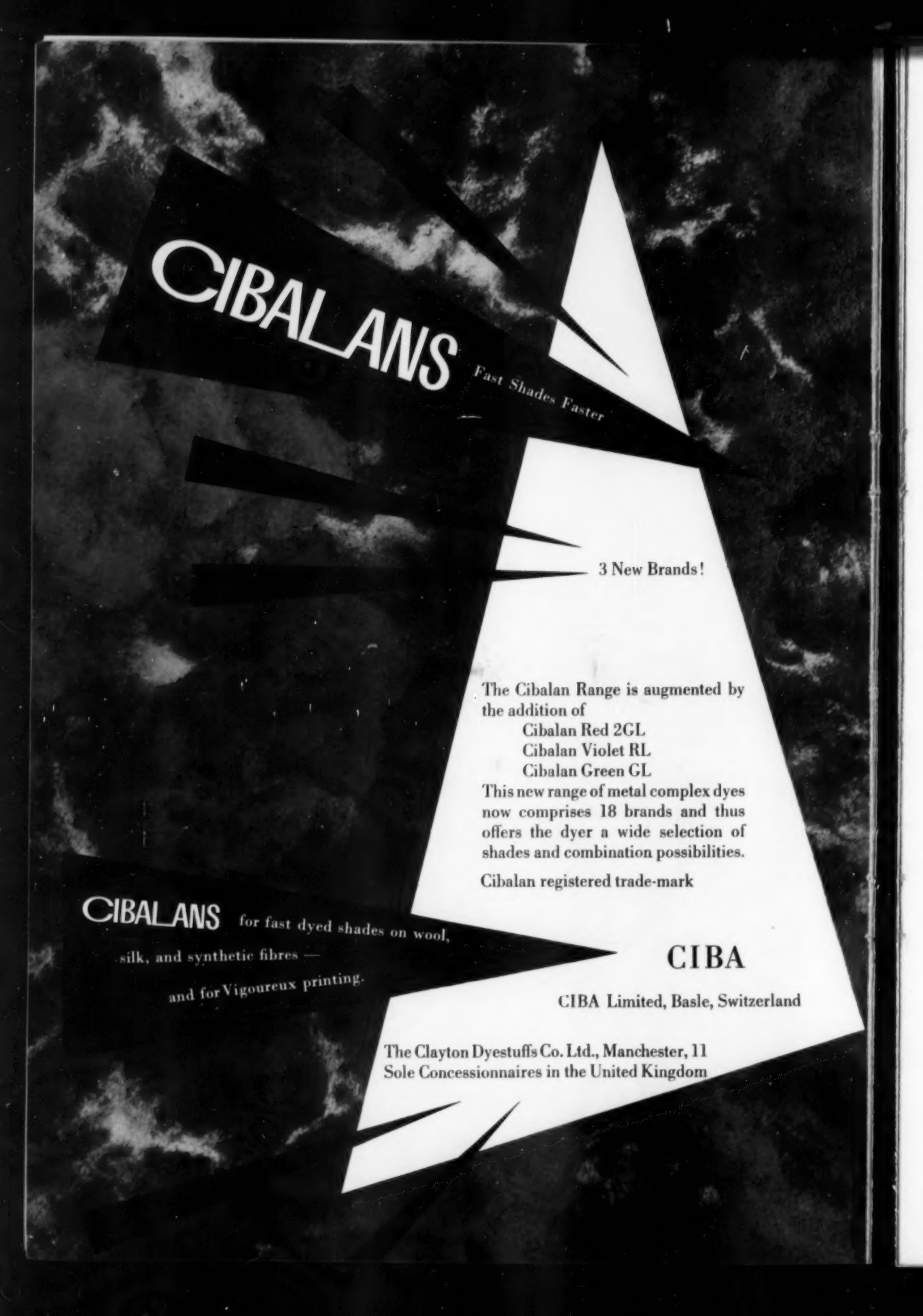
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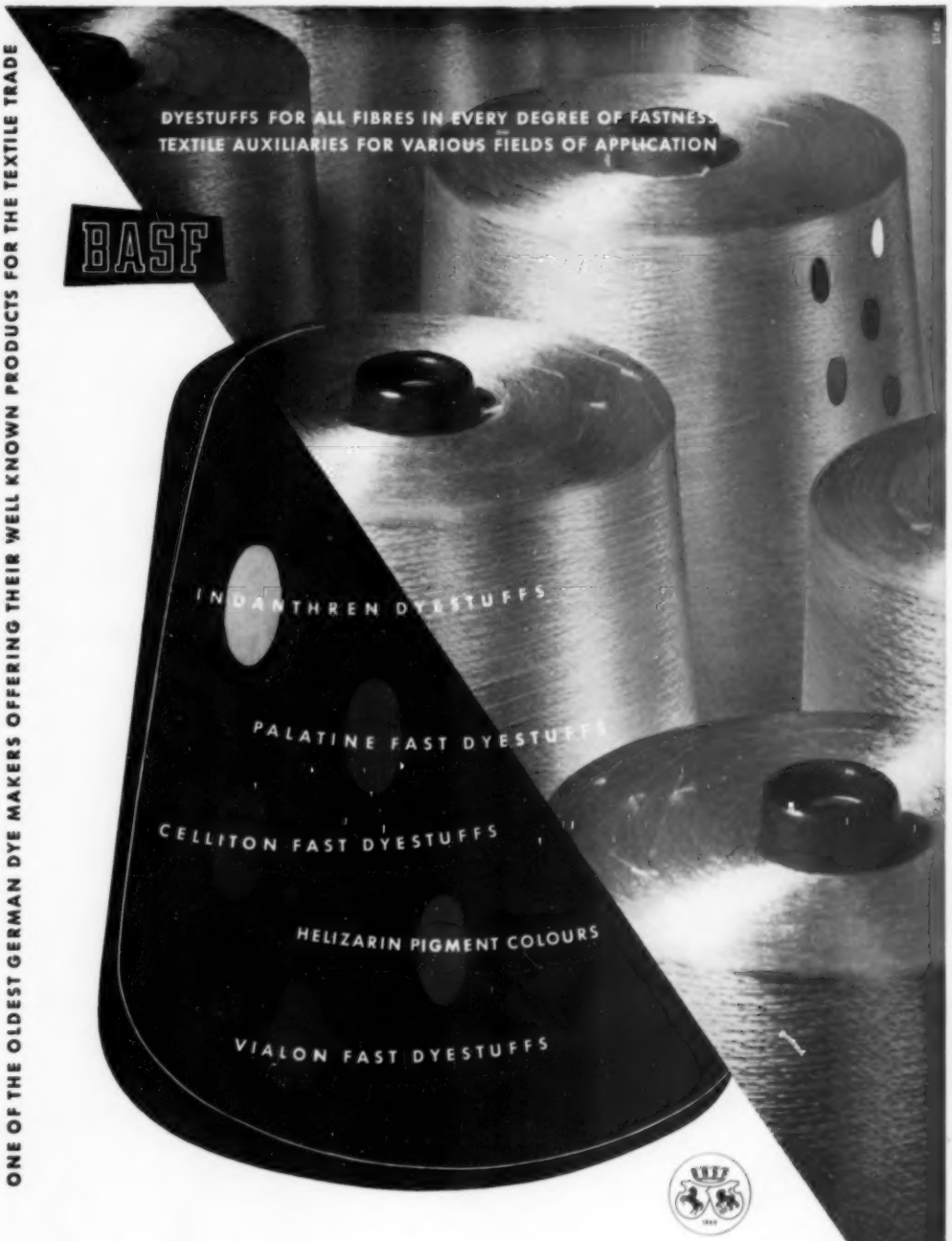

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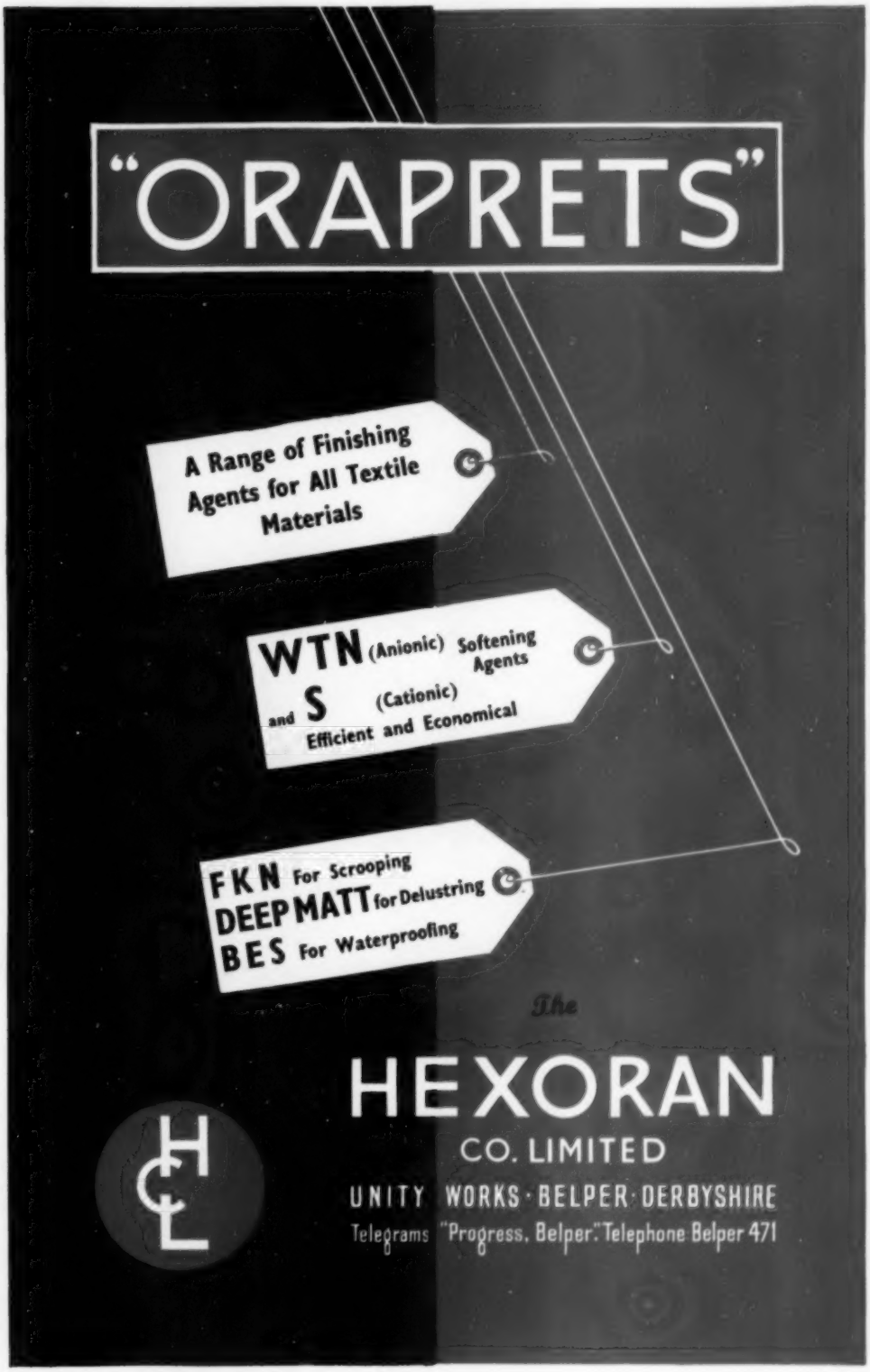
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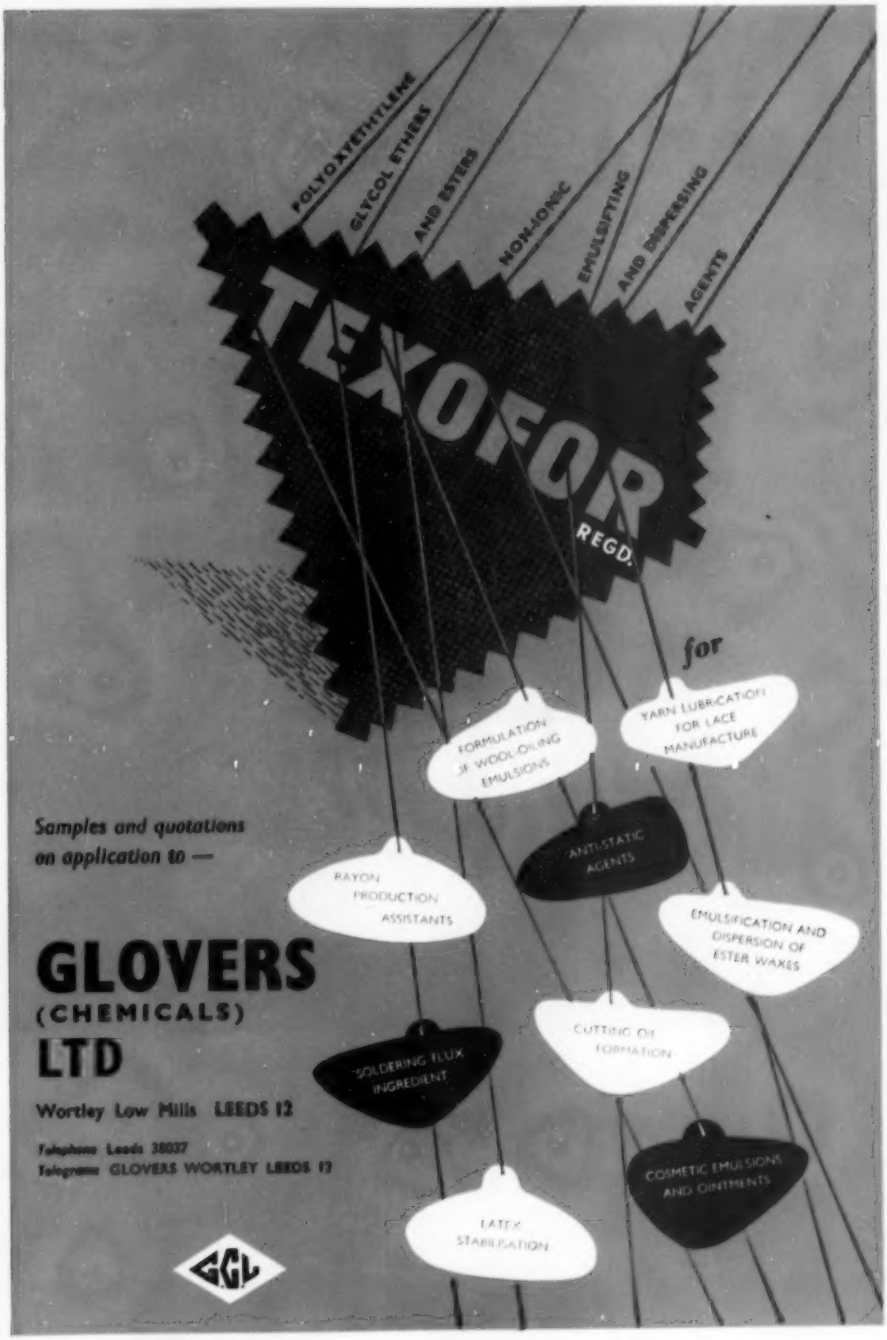
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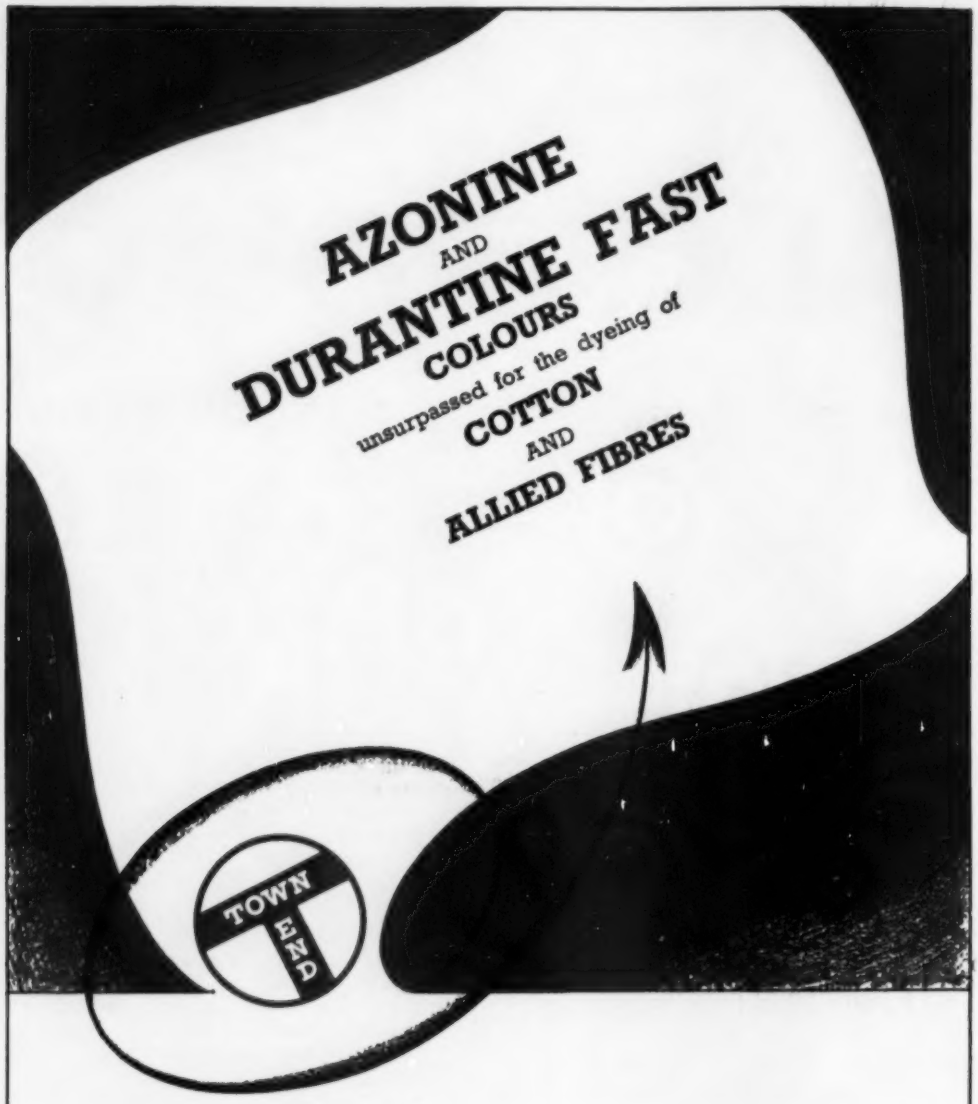

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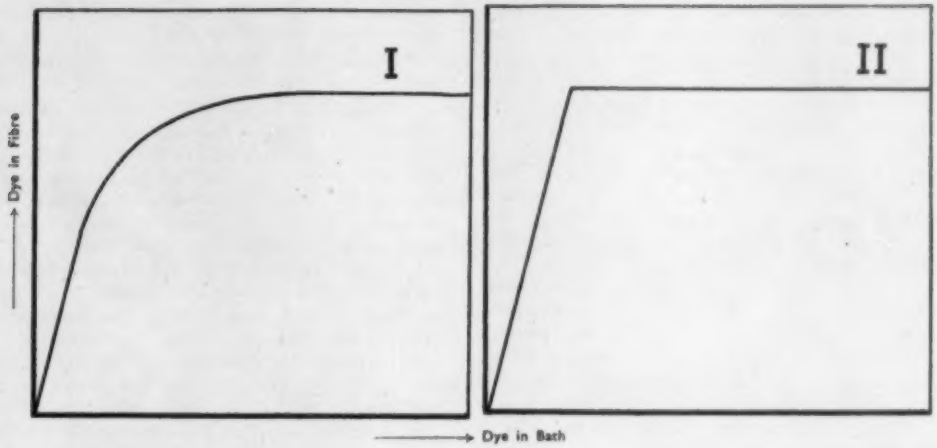


FIG. 1

fibre the curve will consist of two straight lines (type II). It was not suggested that the obtaining of a curve of the first type forms a specific criterion of an adsorption mechanism and, although Vickerstaff and Waters obtained such a curve, they considered that it was probably not to be interpreted on a simple adsorption theory. Recent investigators, however, have established isotherms of type II for the absorption of a number of disperse dyes by acetate rayon, nylon, and Terylene[2–5], and the obtaining of these isotherms has been generally assumed by these workers, mainly on the basis of analogy with the partition of a solid solute between two immiscible solvents, to form a specific indication of "solid solution".

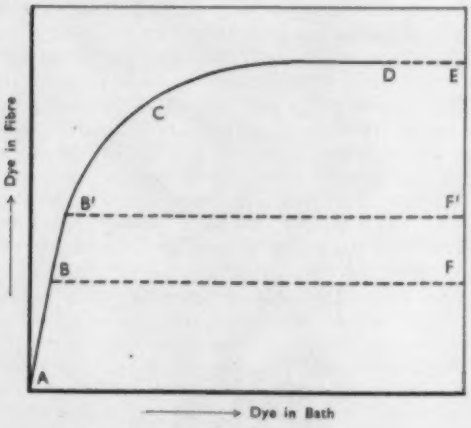


FIG. 2

Let us consider, however, a dyeing isotherm of the Langmuir form *ABCD* (Fig. 2), such as may be obtained, for example, in the dyeing of wool with an acid dye at low pH. This form of isotherm is, of course, associated with adsorption in the fibre at a definite number of sites, substantially independent of one another and approximately equivalent with respect to energy of adsorption, which is generally high. The portion *CD* of the isotherm, where *D* corresponds to a solution of dye that is in equilibrium with solid dye, represents an approach to site saturation in the fibre— a state, however, that can never be completely attained. This unattainability of site saturation is readily shown from statistical considerations; it follows also from the equation for Langmuir adsorption—

$$\theta = \frac{ka}{1 + ka}$$

(θ is the fraction of the sites occupied, a is the activity of the dye in the aqueous phase, and k is a constant), from which it will be seen that at site saturation ($\theta = 1$) the activity of the dye in the aqueous phase would be infinite. The point *D*, therefore, represents thermodynamic saturation with respect to solid dye, but not absolutely complete saturation of sites in the fibre.

In the general case, the curve *ACE* represents a two-phase system consisting of dyed fibre in equilibrium with dye solution. In any such system the tendency of dye to escape from its phase must be the same in both phases, and, taking the chemical potential as a convenient measure of this escaping tendency[6], we may describe the curve also as the locus of points representing pairs of phases of equal chemical potential with respect to dye, and it can be considered quite apart from the third phase, solid dye. The system has analogies with simpler systems, such as aqueous solutions of barium sulphate or ammonium magnesium phosphate, in which the thermodynamic properties of the system can be discussed and even measured up to a concentration that is hundreds of times as great as the solubility of the substance. We can say, in fact, that every dyeing system of the type under consideration has a two-phase equilibrium curve of the form *ACE*; if solid dye happens to have a chemical potential equal to that of the dyed-fibre–solution system represented by the point *D*, the dyeing isotherm will extend to *D*, and we shall attain a state of equilibrium between solid dye, dye in aqueous solution, and a fibre phase in which

almost every available site is occupied by a dye molecule; if, however, the solid dye has a much lower chemical potential, equal to that of a system represented by the point B, in which only a small fraction of the sites is occupied, then the isotherm will consist of *AB*, which is substantially linear; and *BCE* will represent the part of the isotherm that is not realisable in presence of solid dye. Thus, dyeing from a suspension of such a dye would be characterised by an isotherm of the form *ABF*, which, in spite of the fact that dye proceeds by adsorption at sites, is of type II.

There is no inherent improbability in this latter type of system, and, although the writer knows of no experimental evidence that will decide whether it is found in dyeing systems, some remarks on the conditions under which it may occur may be of interest. The chemical potential μ of any component of a system can be expressed as the sum of energy and entropy terms ($\mu = \bar{H} - T\bar{S}$, where $\bar{H}$ is the partial molal heat content and $\bar{S}$ the partial molal entropy of the component under consideration). In the case considered (Langmuir adsorption) the energy change in the fibre for a given increment of dye concentration is the same at all points of the isotherm, and if only energy changes were considered, then according as the energy of dyeing is greater or less than the energy of crystallisation from solution, either the whole of the sites in the fibre would fill up at the expense of dye crystals, or the fibre would not dye at all (chemical potential independent of concentration of dye in fibre). However, owing to the statistical nature of adsorption, which is expressed, for example, in the chance of a dye molecule finding a given site vacant, the differential entropy of dyeing changes rapidly as the sites become occupied, leading to a continuous increase in chemical potential; also, the entropy of the solid dye (relative to a standard vapour state) will vary from one dye to another. It may be conjectured (with no better justification, perhaps, than that many of us are a little hazy about entropy and would prefer to deal with more tangible quantities) that the variation of the entropy term from one dye to another may be much less than that of the energy term, in which case the question is largely resolved into a consideration of differences in the forces holding the dye in the fibre, and in the crystal. If the latter are more powerful than the former, then we may very well expect to have a dye crystal having a much lower chemical potential than that of dye in the fibre at a state approaching site saturation. It is certain that the relation between the systems of forces present in these two phases is not necessarily a close one, and it is possible, for example, that two isomeric dyes could be found that would give systems following identical courses along *ABCE* (the systems of forces attaching them to the fibre being practically identical), but giving differing isotherms (*ABF* and *AB'F'*) owing to the fact that a slight constitutional difference, say in the position of a methyl group, results in an appreciable difference in the readiness with which the dye molecules pack together in their respective crystals— this would result in a difference in lattice energy and therefore in chemical potential, which would account for the differing "solubilities" in the fibre (which would be proportional to the solubilities of the dyes in water).

Our starting point in this discussion was the antithesis between solid solution and adsorption, only one type of which has been considered. It is doubtful, however, whether a distinct line can, in fact, be drawn between solid solution, understood as a system in which absorbed dye molecules have an appreciable degree of mobility and are attached to the substrate by relatively weak and variable forces, and various systems in which dye-molecule sites— a term that has some meaning even in our picture of solid solution— are more defined, more enumerable, and usually of greater affinity for dye (the extreme case being Langmuir adsorption); but, if the chemical potential of solid dye is much less than that which the dye would have when present in the fibre at a state approaching site saturation, then all these systems will give equilibrium isotherms of precisely the same form.

However, some, following the analogy of liquid partition systems, appear to understand the term "solid solution" as any system in which the adsorption curve is a straight line passing through the origin. In that case the term is of little practical or theoretical value— thus the initial stages of adsorption would be described as solid solution, irrespective of the physical basis of the process. The fact is that adsorption and solid-solution systems, as I have defined them, are in like measure analogous to liquid solutions, though the analogies are not perfect— liquid solutions exist in which all solute molecules are firmly attached to one or more solvent molecules, and an analogous system in which the solvent is a solid, having in our case a very large "internal surface", is referred to as an adsorption system; other liquid solutions exist in which the attachment between solvent and solute molecules is not so firm, and the analogous solid system may be termed "solid solution".

The picture given here is far from complete. For example, other substances are present during dyeing, and the effects of these and of water— as swelling agents, solubilising agents, protective colloids, competitors for "sites", etc.— must be taken into account; but their presence does not affect the main argument and a full discussion will not be given here.

The purpose of this communication is not to discuss whether the dyeing of disperse dyes on various fibres may be better described as adsorption, as solid solution, or as one of these processes complicated by further, e.g. colloidal, effects, but to point out that the obtaining of a linear isotherm of type II provides no criterion of the way in which the system is to be described, and, it is hoped, to stimulate some thoughts on dyeing mechanisms by clothing some of the old notions in new dress.

A. E. Stubbs

Research Laboratories
Bleachers' Association Ltd.
Bromley Cross
Bolton

10th December 1953

[1] Vickerstaff and Waters, J.S.D.C., **63**, 116 (1942); Vickerstaff, *The Physical Chemistry of Dyeing* (London: Oliver & Boyd, 1950), p. 262.
[2] Daruwalla and Turner, J.S.D.C., **69**, 240, 440 (1953).
[3] Bird, Manchester, and Harris, *Discussions of the Faraday Soc.*, No. 16, 85 (1954).
[4] Schuler and Remington, *ibid.*, No. 16, 201 (1954).
[5] Wahl, Arnould, and Simon, *Teintex*, **17**, 288 (1952).
[6] Vickerstaff, *op. cit.*, p. 96.

Synthetic Fibres

I have companion-like affection for Mr. H. à Brassard's purist crusade [1] (lively albeit synthetic), but I find difficulty in correlating the principle he would establish with the definition propounded by *Chambers's Twentieth Century Dictionary*, namely—

> a term applied to the building up of compound substances from the elements they contain or from other compounds, usually of less complexity than themselves; a making a whole out of parts.

G. S. Marr

Edward Lee Ltd.
Victoria Dyeworks
Burnley
Lancs.
9th January 1954

Mr. à Brassard [1] is, I think, a little too concerned about the purity of the term "synthetic" and seems to wish to restrict its use to describe an exact equivalent of a natural product. My own dictionary [2] is less strict and recommends the use of the word for substances made by chemical processes and of a like nature to naturally occurring ones. This meaning is widely accepted; thus, indanthrone is a synthetic dye, aspirin is a synthetic drug, and synthetic resins, detergents, and tannins have no exact counterparts in Nature.

If substance A reacts with substance B, neither being fibrous in character, to produce a substance which is fibrous, then it seems fair to say that a synthetic fibre has been produced— not synthetic wool nor synthetic cotton, perhaps, but still a synthetic fibre.

Mr. à Brassard's proposed "chemical fibre" seems to mean something rather different; it suggests a fibre used in the processes of chemistry, as a "medical fibre" would be used in medicine. Chemical plant, chemical laboratory, chemical labourers have this sense. Synthetic labourers have not yet appeared, but I think we may be satisfied that we have all seen synthetic fibres.

Ernest Stead

1 Eden Road
Kirkstall Hill
Leeds 4
13th January 1954
[1] J.S.D.C., **69**, 496 (Dec. 1953).
[2] *Chambers's Twentieth Century Dictionary*: New Mid-century Version.

The Effects of the Soaping Aftertreatment on Vat Dyeings [1]

Since the submission for publication of the above paper, in which the conclusion was reached that the observed changes in colour, etc. could be attributed to crystallisation of the dye in the fibre during the soaping process, another paper on the same subject has been published [2].

In the latter, the author considers that crystallisation is not the factor which causes the change of colour, a suggestion based on observations of the dichroism of the dyes in the crystalline form and on the soaped fibre. However, the results given for the dichroic behaviour of the dyes in the soaped condition do appear, with one exception, to support the theory of crystallisation.

The exception is Cibanone Yellow GK (Ciba), which is reported as showing negative dichroism on soaping and positive dichroism in the crystal. In our measurements on the equivalent compound, Caledon Yellow 3G (ICI), it was found that in the soaped form the dye showed positive dichroism, which is in agreement with that shown by the crystal.

That the colour changes are due to differences in the degree of polarisation of the dye molecules seems to be well substantiated, but it also appears reasonable to suggest that these changes in polarity could be caused by intermolecular crystalline forces.

H. H. Sumner
T. Vickerstaff

Imperial Chemical Industries Ltd.
Dyestuffs Division
Hexagon House
Manchester 9
18th November 1953
[1] Sumner, Vickerstaff, and Waters, J.S.D.C., **69**, 181–194 (June 1953).
[2] Wegmann, *Textil-Rundschau*, **8**, 4–9, 97–108, 157–165 (1953).

Notes

Meetings of Council and Committees

February

Council— 17th
Finance— 17th
Publications— 16th
Colour Index Editorial Panel— 25th
Reviews of Textile Progress— 19th
Joint Conference with Textile Institute— 19th
Society's Medals— 24th
Perkin Centenary— 8th

John Warner Nicholls
Secretary to the Society

The Council of the Society announces the appointment of Mr. John W. Nicholls, F.C.I.S., as Secretary. Previously the position of Editor and General Secretary was held by Dr. C. J. W. Hooper, but, owing to increasing activities of the Society, it has been decided to divide the duties. Therefore, Dr. Hooper will now assume the position of Editor and Technical Officer, and Mr. Nicholls that of Secretary to the Society.

Mr. Nicholls was formerly National General Secretary, in London, of the Institution of Works Managers, which incorporates the Institute of Factory Managers and the British Works Management Association. He is qualified as a Fellow of the Chartered Institute of Secretaries and a Government Public Relations Director. During the war he served with the Warwickshire Regiment and the R.A.S.C., both at home and overseas, and he holds the retired rank of Major.

New Books and Publications

Fibres from Synthetic Polymers

Edited by Rowland Hill. Pp. xv + 554. Amsterdam: Elsevier Publishing Co., 1953. Price, 80s. 0d.

There have been several excellent books recently on the fundamentals of polymerisation reactions, and a number of books dealing with the technology of synthetic fibres, but this book attempts a synthesis of the two fields of study. Its aim, in Dr. Hill's own words, is "..... to present an authoritative and balanced account which will serve to advance understanding . . . by stressing principles as well as facts. The subject is treated wherever possible with a major emphasis on the theoretical aspects, combining these where appropriate with the more practical implications and consequences as they arise." This aim has been admirably fulfilled, and Dr. Hill's team of eighteen authorities has fashioned a work which has a unity of purpose and expression that is often lacking in co-operative literary enterprises.

The title accurately defines the limits of the book, since only those totally synthetic fibres which are manufactured by the chemical industry are included. There are 184 pages on the synthesis, and 131 pages on the structure and texture, of fibre-forming polymers, 86 pages on the conversion of polymers into fibres, and 123 pages on fibrous properties and dyeing characteristics. From these figures it will be seen that a reasonably well balanced account of the subject has been given, allowing for the avowed stress on theoretical aspects.

Turning now to the individual chapters, Dr. R. Hill summarises in a short introduction the historical development of high polymers, and indicates how the chemical structure of a polymer determines whether it will be a resin, rubber, or a fibre. Prof. H. W. Melville has written a brief but comprehensive outline of the mechanism of vinyl polymerisations, showing how the kinetics of such reactions are determined. The rôle played by such factors as bond strengths and resonance energies in determining the course of vinyl polymerisations is described by the late M. G. Evans. Practical aspects of the formation of fibre-forming vinyl polymers are covered in the next chapter, which deals with the polymerisation of ethylene (R. B. Richards), acrylonitrile (L. B. Morgan), and vinyl and vinylidene chloride (I. Harris).

R. J. W. Reynolds contributes three chapters on polycondensation, of which the first, outlining the principles of polycondensation, is the least satisfactory. The degradation of polymers, the polymerisation of ring compounds such as caprolactam, and monomer–polymer equilibria are all topics that merit a more quantitative treatment. On the other hand, what may be described as the preparative organic chemistry of polycondensates is most admirably dealt with in the next two chapters, which cover in detail those polymers which have already reached industrial production and in outline those polymers which are so far of only academic interest.

Molecular weights and molecular weight distributions influence the properties of polymers markedly, so that it is only proper that their measurement should be described in a chapter by F. D. Hartley. C. W. Bunn contributes four chapters on the structure and texture of polymers, two of which, those dealing with molecular structure and the structure of crystalline regions, might profitably be fused into one, since their subject matters overlap to a considerable extent. The remaining two chapters cover the determination of the proportions, sizes, and orientations of amorphous and crystalline regions, and the relations between these factors and the cold-drawing and melting of polymers.

After a chapter by E. E. Walker on the theory of the solution of polymers, there follow three short chapters on the melt (R. M. Lodge), wet (J. M. Preston), and dry (W. Frey and A. Sippel) spinning processes; the use of unlabelled graphs in Chapter 14 is very irritating. The sections which follow on the properties and applications of polyamide (A. R. Munden), polyester (I. Marshall and J. R. Whinfield), and vinyl and acrylic (G. H. Fremon) fibres furnish a useful summary of the properties of synthetics, although the first two do not live up to their comprehensive titles but deal only with nylon 66 and polyethylene terephthalate respectively. G. H. Fremon, in particular, has furnished a lucid and up-to-date account (the literature is covered up to 1952) of an extremely complex field, in which the numbers, properties, and compositions of the starters are altering rapidly. Finally, T. Vickerstaff contributes an account of the dyeing of synthetic fibres.

A descriptive, non-mathematical treatment is used throughout, so that the book reads easily. Sections which the reviewer would like to see expanded in succeeding editions — for this is bound to become a standard work — include those on the mechanism of crystallisation, setting, and the technology of the conversion of polymers into fibres, generally. The book is well printed, with few errors, although the cover is poor, especially in view of the excessively high price. This is a book that should be on the shelves of every textile library and every chemist interested in synthetics, and it is unfortunate that the price will undoubtedly limit its sales largely to institutions.

L. Valentine

Chemische Textilfasern, Filme und Folien

Edited by R. Pummerer. Pp. 1464. Stuttgart: Ferdinand Enke, 1953. Price, DM 194 full cloth, DM 188 paper cover.

This large volume is a collection of a series of articles on chemical textile fibres, films, and foils, their fundamentals and technology. More than thirty experts each contribute an authoritative article in their own specific field with Dr. R. Pummerer, Professor of Chemistry at the University of Erlangen, as editor. The content of this book is rather heterogeneously assembled and

assorted, and the nine single issues, published at intervals since 1951, are now available in one work.

The book is divided into two parts (A) "Chemical Textile Fibres" (pp. 7–1161) and (B) "Films and Foils" (pp. 1162–1401); there is also an author and firms index (pp. 1402–1416) and a well compiled subject index (pp. 1417–1464).

Part A deals with cellulosic fibres, the molecular and macromolecular structure of cellulose, with the structure and manufacture of regenerated cellulosic fibres, and with the alginate, protein and synthetic fibres. After this sometimes rather lengthy discourse on the structure and manufacture of cellulose and synthetic fibres, follow papers on the sizing of rayon and synthetic fibres and on the dyeing, printing and finishing of textiles. In studying the articles in this section of the book (pp. 762–1022) one feels that some of the authors have had very little experience in the handling and processing of textiles. The dyeing and printing methods they describe can be studied more advantageously in a text-book, and some of the recent publications of English and American authors present a more up-to-date account of modern dyeing, printing and finishing methods. After an article on glass fibres Part A concludes with two papers on chemical, physical and mechanical-technological testing methods of fibres. The three chapters (X–XII) on this subject are very informative and well written.

Part B consists of three sections on the testing of plastic films; the properties and manufacture of films and sheets of cellulose esters; and of films and foils of synthetic material.

It must have taken a considerable time to write and to collect the various papers, some of which must have been written many years ago; chapter XI was concluded in January 1949. Whilst the book contains many references to patents and literature, in many cases recent publications are not mentioned at all and even books which were published by German and other Continental authors, such as Mecheels, Weiss, and Luniak, are omitted. The whole volume lacks co-ordination and uniformity; almost every contributor uses his own method of quoting references. It contains much useful information but hardly any of the 33 articles are original in subject matter. It might be permissible to draw the attention of our Continental colleagues to some of the recent publications by American and British authors on textile technology and synthetic fibres, most of which provide such excellent and up-to-date information. We would also recommend the study of the *Annual Review of Textile Progress*, published jointly by the Textile Institute and our Society.

On the whole Professor Pummerer's effort is disappointing, but it will provide a useful book of reference. A. F. KERTESS

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., **68**, *23 (Jan. 1952), and also, together with symbols and the periodicals abstracted, in the annual index*

I—PLANT; MACHINERY; BUILDINGS

PATENTS

Continuously After-treating Freshly-spun Artificial Filaments. A. Maurer. *BP* 701,313

Liquor flows through conduits so arranged that the flow of the liquor causes the filaments to pass through the conduits without use of driven rollers. The conduits have enlargements to cause the filament bundle to open and close repeatedly along the conduits thus reducing the time required for treatment. C. O. C.

Thread Storage, Thread Advancing Device. Courtaulds. *BP* 701,801

Setting up of the thread on the device is facilitated by there being in the device at least one roller having a barrier which impedes the advance of the thread and a guide which can lie out of the path of the thread and can be moved into the path of the thread to assist it to pass the barrier. C. O. C.

Preparing Freshly Spun Cakes of Rayon for After-treatment. Algemene Kunstzijde Unie. *BP* 702,550

Modification of *BP* 674,535. The inner end of a spiral of rigid sheet material is connected to a rotatable shaft. When the shaft rotates the permeable member wraps over the spiral and then the cake is placed on it. The shaft is then rotated in the opposite direction so that the permeable member is unwound and as it expands engages firmly the inner walls of the cake. C. O. C.

Automatically Mixing and Feeding Dyes to Dyeing Vessels. S. Converse and C. M. McKeown. *USP* 2,630,002

Rate of travel of cloth or a warp through the box of a pad automatically controls the addition of dye liquor from a storage tank and also the addition of the various ingredients to the storage tank. C. O. C.

Accelerating and/or Intensifying the Action of a Liquor on Fibrous Materials by Use of Vibrations. F. Früngel. *BP* 701,476

The liquor is agitated by a vibratory device excited by a rotary unbalanced mass within the device so that radially directed faces are introduced into the liquor, these forces changing their directions continuously in synchronism with the rotational speed of the unbalanced mass. C. O. C.

Wet Processing of Yarn in Cheese Form. A. Noseda. *BP* 702,679

A support placed at the bottom of the vat has several treatment units arranged on it. Each unit has a tubular perforated column fixed to the support and is formed so that several cheeses can be slotted into it. A tubular perforated wall concentric with the column is placed around the cheeses after they have been put into position. C. O. C.

Controlling the Degree of Stretch of Yarn in a Yarn Sizing Machine. Thomas Holt. *BP* 702,522

Continuous Heating of Textiles by Infra-red Radiation. Raduner & Co. *BP* 700,883

A housing has an infra-red radiating ceiling and a support for the goods which contains several compartments. Each compartment has a regulator so as to give the surface of the compartment a predetermined temperature. C. O. C.

Drying Continuous Lengths of Yarns, Tapes, etc. American Cyanamid Co. *BP* 701,675

A hollow stationary cantilevered shaft extends lengthways within a cantilevered rotatable hollow drying roll. The shaft is fitted with an electrical heating unit so designed that there is greater concentration of heat at the feed on end of the roll than at the take off end. The yarn, etc. proceeds spirally along the roll from one end to the other. C. O. C.

Blowing Nozzles for Treating Fabrics, Paper, etc. J. Dungler. *BP* 702,813

The fabric, etc. is supported by rollers above each of which there is a nozzle which delivers at least two individual jets of air or the like. These jets not only press the material against the roller but are so directed that the zone of impact of at least one of the jets is substantially different from the zones of contact between the strip material and the supporting roller. By this means the material does not become displaced laterally and the air passes through the material being treated. C. O. C.

Preventing and/or Eliminating Strain in Fabrics during Handling or other Treatment on a Flat Surface. C. A. Kindstrand. *BP* 701,158

When fabric is treated in such a manner that part of it rests on or is moved across a plane surface, tension set up by contact of the fabric with this surface is reduced or eliminated by causing the surface to vibrate horizontally and/or vertically. C. O. C.

Friction Calender of the Endless Carrier Band Type. P. Deck. *BP* 701,401

The difference between the speed of the carrier band and the drum is kept constant if there is in addition to the carrier band round the driving cylinder, a driving band which follows the arc of the carrier band where it extends round the cylinder. This driving band is driven at the same surface speed as the cylinder and is applied by resilient pressure against the carrier band. This ensures that the carrier band constantly maintains the tangential speed of the cylinder. C. O. C.

Safety Device for Use on Calenders. John Boath Junior & Co. *BP* 701,404

In a calender used for cheating (i.e. where the material is wound upon one of the rollers) a safety member is placed near to the nip and in association with a chesting blade. The safety member and the blade are so arranged that the safety member is moved to and from the nip as the blade moves from and to the nip respectively. In normal working this safety member, e.g. a roller whose diameter is small compared with that of the calender rollers, is maintained in the nip just clear of the material being wound onto the calender roller. C. O. C.

Drying Wool Cloth. J. P. Stevens & Co. *USP* 2,629,940

The cloth is led at open width in several runs through a drying chamber through which a large volume of hot air is passed from side to side throughout an area coextensive with the area traversed by the runs of cloth. This air is not recirculated. This ensures that the drying air is always at low R.H. with consequent high drying capacity. The cloth is left with high regain capacity and in its natural state. The consumption of steam can be reduced to half that used by other drying processes. C. O. C.

Safety Devices for Fabric-steaming and like Machines. William Whiteley & Sons. *BP* 701,094

If the worker's arm is drawn in towards the rotating roller it actuates a lever mechanism which in turn operates a switch which applies braking current to the driving motor so as to stop the machine. C. O. C.

Coating Paper, Textiles, Metal Foil, etc. with Polyethylene, etc. DuP. *BP* 701,553

Modification of *BP* 688,637.

The polyethylene or other synthetic linear polymer used is prevented from adhering to any rubber roller used by coating the roller with polytetrafluoroethylene. C. O. C.

Producing Bleed Lines Around Designs on a Printing Surface. Mergenthaler Linotype Co. *USP* 2,630,384

Machines for Attaching Identifying Labels to Fabric or Garments. G. J. Sutton. *BP* 701,437

A machine which forms, attaches and prints the tab without damaging the fabric to which the tab is attached. C. O. C.

Loosening Household Linen after Hydroextraction. D. and J. Tullis. *BP* 702,485

Control Apparatus for Laundry Drying and/or Ironing Machines. Baker Perkins. *BP* 702,147

A device for ensuring that a multiple roller ironing machine always works at optimum speed. C. O. C.

Drying and/or Setting Rabbit and other Fur-bearing Skins. S. W. Howarth. *BP* 702,330

The skins are held flat during drying and/or setting by pressing them against a surface by air pressure. This obviates need for mechanical devices to hold the skin with the danger of damage to the fur and interference with uniform drying of the skin and consequent failure of the skin to dry flat. C. O. C.

III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Wool Wax. IV—The Constitution of the Aliphatic Diols. D. H. S. Horn and F. W. Houger. *J.C.S.*, 3533–3538 (Nov. 1953).

Five alkane-1:2-diols have been isolated, by chromatography and distillation at reduced pressure, from the unsaponifiable fraction of wool wax. They are identified, from infra-red studies and by degradation to fatty acids of known constitution, as *n*-hexadecane-, 16-methylheptadecane-, 18-methylnonadecane-, 20-methyleneicoxane-, and 22-methyltricoxane-1:2-diol. No other diols could be detected. H. H. H.

PATENTS

Detergent. Basf. *BP* 701,805

Mixtures of surface active substances and high mol-wt. nitrogenous polymers, e.g. polymeric *N*-vinylpyrrolidone or polymeric ethyleneimine, are excellent detergents for textiles. Presence of the nitrogenous polymers causes quicker, higher and more stable foaming and also prevents bleeding of dyes. C. O. C.

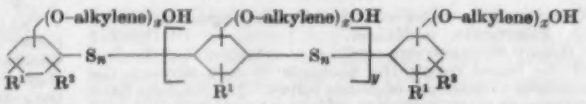
Wetting, Detergent and Levelling Agents. Petrolite Corpn. *USP* 2,629,704–6

Phenol–aldehyde resins derived from aldehydes of <9C and phenols of formula—

(R = hydrocarbon of 4–14C, R being in either *o*- or *p*-position) are oxylated with both ethylene oxide and propylene oxide to yield wetting, etc. agents. C. O. C.

Polyglycol Ethers of Alkyl Phenol Sulphides—Wetting, etc. Agents. General Aniline. *USP* 2,629,743

Compounds of formula—



(R^1 = Alk; R^2 = H or may if $y = 0$, = Alk; total number of Alk C atoms in $R^1 + R^2$ in any benzene nucleus = 6–18; n = 1–4; $y < 5$; $x = 70$) have good wetting, washing and emulsifying properties. C. O. C.

Polymeric Polyacids—Auxiliary Agents, etc. DuP. *BP* 701,124

The products obtained by copolymerising ethylene with butene-1:4-dioic acid monoester under pressure and at 0–250 c. in presence of a compound yielding unstable free radicals under the conditions of reaction have a wide variety of uses, e.g. as antislip agents for regenerated cellulose film, insolubilising agents for dyes, water-repellents, plumping agents and lacquer finishes for leather, carbon paper ink, hair curling agents, binders for ceramic finishes on glass, detergents in non-aqueous systems, water repellents for textiles pretreated with polyamines, etc. C. O. C.

Warp Size. Stein, Hall & Co. *USP* 2,630,416

A size free from dusting, of high affinity for both natural and synthetic fibres, very stable especially as regards viscosity and with no tendency to decompose or putrefy, consists of an aqueous solution of an alkaline boron salt reacted with a copolymer of styrene or substituted styrene with maleic anhydride or an incompletely esterified maleic anhydride. C. O. C.

Resin Size for Textiles. Manufactures de Produits Chimiques du Nord Etablissements Kuhlmann. *BP* 701,655

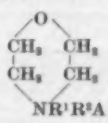
Siccative resins formed of unsaturated hydrocarbons of high iodine number and high mol. wt. obtained in refining natural or synthetic petrol are excellent sizes for rayon. They have the advantage that in their removal the rayon recovers its original characteristics without any loss in strength such as occurs when drying oil sizes are used. C. O. C.

Polymers of Formals—Auxiliary Agents. DuP. *USP* 2,630,424

Linear formals containing two or more OH and/or OCH_2O groups can be polymerised to give products having a wide range of physical and chemical properties by contacting them with a suitable catalyst, preferably an acid catalyst. The conditions of polymerisation may be widely varied between −80 to 300°c. and pressures up to 100 atmospheres or more. The products have many uses, e.g. as textile sizes, permanent finishes, components of printing inks, plasticisers, fur mordanting, rendering leather fat resistant, etc. C. O. C.

Antistatic Agent. Atlas Powder Co. *BP* 702,089

Materials of formula—



(R^1 = Alk of 11–20 C; R^2 = Alk of 1–5 C; A = anion) are applied in aqueous solution as antistatic agents. C. O. C.

Tanning Agents, Dye Intermediates, Agents for Reserving Wool, etc. Basf. *BP* 701,103

The water-soluble products obtained by the hot condensation of addition compounds of bisulphites and saturated aliphatic keto- or aldehydo-methylene compounds with substituted or unsubstituted formaldehyde or phenols have a wide variety of uses, e.g. as tanning agents, dye intermediates, reserving of wool, lake manufacture, etc. C. O. C.

Improving the Fastness to Wet Processing and Light of Direct Dyes. Gy. *BP* 702,695

The polymers obtained by reacting aliphatic tertiary polyamines with aliphatic dihalides are suitable, especially in combination with soluble copper compounds, for the aftertreatment of dyeings with direct dyes. With most direct dyes considerable improvement in wet fastness properties results and with many of them improvement also in fastness to light. C. O. C.

Acylated Aromatic Trifluoromethylarylaminosulphonic Acids—Mothproofing Agents, etc. Variapat. *BP* 702,602

Acylation of aromatic or heterocyclic aminosulphonic acids containing an exchangeable H atom at the N atom, the components being so chosen that the end product contains at least one trifluoromethyl group, a sulphonic acid group and a diphenyl, diphenyloxide, diphenylsulphide, diphenylsulphoxide, diphenylsulphone, diphenylmethane, diphenylcarbamide or stilbene radical yields colourless water-soluble products which are useful as mothproofing agents and for protecting all kinds of textiles against pests. The mothproof they impart is fast to scouring and milling. When suitably substituted they may also be used as rotproofing agents. C. O. C.

Flame Resisting Agent. Monsanto. *BP* 700,822

The products obtained by reacting phosphorus oxychloride with ammonia first at < 100°c. and then to 110–150°c., have mol. wt. 180–300 and yield alkaline solutions in water. They are suitable as flame-resisting agents, particularly for cellulosic materials, a wash-fast effect being obtained by impregnating with the aqueous solution, drying and then baking at 100–200°c. C. O. C.

Phenol–Aldehyde and Ketone–Aldehyde Condensates—Textile Finishes. Borden Co. *USP* 2,629,703

A mixture of a ketone–aldehyde (prepared from a ketone of formula CH_3COR (R = Alk of 1–4 C) and an aliphatic aldehyde of < 5 C) and a potentially active phenol–aldehyde condensate can be cured to resin. Such a mixture has wide uses, e.g. as casting resins, adhesives, impregnating textiles, etc. C. O. C.

Stabilised Polyvinyl Acetate Emulsions as Textile Finishes. H. L. Snyder. *USP* 2,629,702

Emulsions containing polyvinyl acetate and a styrene-butadiene copolymer can be prepared of high concentration and can be diluted with water without impairing their stability, in addition they are stable to agitation and foaming. The finish they impart to textiles is more enduring, more wash resistant and more pliant than that imparted by polyvinyl acetate alone. C. O. C.

Chlorosulphonated Polyethylene as Adhesive for Bonding Fabrics. DuP. *USP* 2,630,398

Uncured chlorosulphonated olein polymers are useful adhesives for bonding fabrics together by means of heat and pressure. The polymers are cured by heat in absence of any vulcanising aid. C. O. C.

Paint and Varnish Remover. DuP. *USP* 2,630,409

A mixture of 1 : 1 : 2-trimethoxyethane and an aromatic hydrocarbon, alkane or chloroalkane is used, e.g. 1 : 1 : 2-trimethoxyethane (100 parts by wt.) and benzene, toluene, or ethylene dichloride (10–100). The mixture has low volatility combined with excellent film-dissolving properties. C. O. C.

Alkyl Aryl Sulphonate—Liquid Hydrocarbon—Aliphatic Hydroxy Compound Compositions—Printing Inks, Paints and Dry Cleaning Agents (V p. 133).

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Vat Dyes. III—Acyl and Aroyl Derivatives of 2 : 7-Diaminophenanthraquinone. R. D. Desai and R. H. Kundel. *J. Sci. Ind. Research* (India), **12B**, 234–5 (1953): *Chem. Abs.*, **47**, 12819 (25 Nov. 1953).

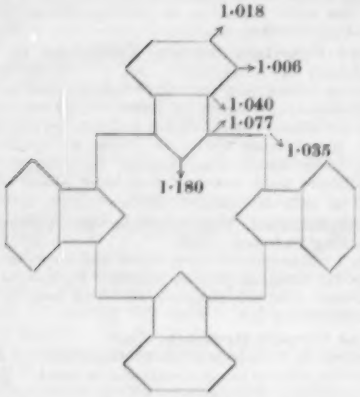
Diaminophenanthraquinone (2g.), valerylchloride (2·4) and dry nitrobenzene (50 c.c.) were refluxed for 5 hr. when a 65% yield of 2 : 7-bis(valerylamino)phenanthraquinone separated out as small dark brown needles; it could not be vatted. The following derivatives were similarly prepared from diaminophenanthraquinone and the corresponding acid chloride (only the acyl or aroyl radical is given): distearoyl, dark reddish brown plates with no vatting properties; di-3-furoyl, reddish brown plates, which yield a leuco compound having no affinity for cotton; dicinnamoyl, brick red needles, which do not vat; di-*o*-chlorobenzoyl, pinkish needles which do not vat; di-*o*-acetoxybenzoyl, small brown plates which dye cotton pale olive not fast to soaping or bleaching; di-*p*-methoxybenzoyl, dyes cotton pale yellowish olive not fast to soaping or bleaching; bis-(2-hydroxy-3-naphthoyl) dyes cotton greyish olive fast to soaping and of fastness to light and bleach 5 and 2–3 respectively. This last dye yielded a pinkish brown with diazotised *o*-nitroaniline, reddish brown with diazotised 2 : 5-dichloroaniline and bluish violet with tetrazotised dianisidine, the dyeings being fast to light, rubbing and bleaching. C. O. C.

Aminothia-2′-cyanines and their Sensitising Properties. K. Meyer and E. Krietsch. *Z. wiss. Phot.* **48**, 126–136 (1953): *Chem. Abs.*, **47**, 12065 (25 Nov. 1953).

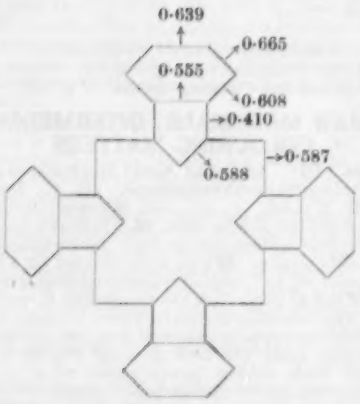
A discussion of methods of synthesis of this group of dyes. Special attention is paid to 3 : 1′-dialkylthia-2′-cyanine iodide (I), 6′-amino-I (II) and 6-amino-I (III). Their sensitising action was tested with a boiled and an ammonia emulsion. III had very little effect in increasing the spectral sensitivity. II was quite effective being superior to I. II + I gave by far the best results in the ammonia emulsion but not in the boiled emulsion. Super-sensitising depends on the emulsion as well as on the dye. C. O. C.

Structure of the Phthalocyanines according to the Homocyclic-conjugation Approximation. A. Pullman and G. Berthier. *Compt. rend.* **236**, 1494–6 (1953): *Chem. Abs.*, **47**, 11827 (25 Nov. 1953).

Principal results of a study of phthalocyanine by the method of linear combination of atomic orbitals are given in A for distribution of charge and in B for bond indices in a hypothetical model with homocyclic conjugation (with the central metallic atom omitted)—



A



B

In this model, the phthalocyanine resembles a porphyrin; 42 π electrons occupy the 21 lowest molecular orbitals in the ground state, leaving 19 orbitals vacant. The change of porphyrin to phthalocyanine is accompanied by a decrease in energy that would result in displacement of the absorption band farthest in the visible. The charge distribution is not uniform, however; concentrations are everywhere > 1, and the greatest accumulation of π electrons occurs on those atoms in the actual compounds having electronegativity greater than that of C. The energies of molecular orbitals are tabulated. C. O. C.

Dye Salts obtained from Cyanines and Erythrosin. Y. Hishiki. *Repts. Sci. Research Inst.* (Japan) **29**, 72–9 (1953): *Chem. Abs.*, **47**, 12067 (25 Nov. 1953).

Mono-, tri- and azomethinecyanine, styryloid, and pinacryptol dyes (all as iodides) were mixed (1 : 1 mol.) with erythrosin (**I**) (as Na salt) in hot methanol (to couple by removing NaI) and then concentrated (or in some cases cooled) to precipitate the following 13 crystallised salts: 1 : 1′-diethyl-2 : 2′-monomethinthiacyanine-**I** (**II**); 1 : 5-dimethyl-2(*p*-dimethylaminostyryl)thiazole-**I**; 1 : 1′-diethyl-2 : 2′-trimethinselenacyanine-**I**; 1 : 1′ : 3 : 3 : 3′ : 3′-hexamethyl-2 : 2′-trimethinindocyanine-**I** (**III**); 1 : 1′-dimethyl-*ay*-diazothiazolocyanine-**I**; 1 : 1′-diethyl-4 : 4′-trimethinquinocyanine-**I** (above are all ionic compounds); (1 : 1′-diethyl-2 : 2′-trimethin-β-naphthothiacyanine)$_2$-**I**; (1 : 1′-diethyl-2 : 2′-trimethinthiacyanine)$_3$-**I**$_2$; [1-methyl-2-(*p*-dimethylaminostyryl)pyridine]$_3$-**I**$_2$; (1′ : 1-diethyl-4 : 4′-monomethinquinocyanine)$_2$-**I**; [1-ethyl-2-(*m*-nitrostyryl)-6-ethoxyquinoline]$_2$-**I** (Pinacryptol Yellow); (1 : 1′-diethyl-2 : 2′-trimethinoxacyanine)$_2$-**I**; (1 : 1′-diethyl-2 : 2′-trimethinquinocyanine)$_2$-**I** (**IV**) (above are all molecular compounds). **III** was completely electrolysed in 50% methanol in 1 hr., the cyanine forming on the cathode and the **I** on the anode. **II** and **IV**, warmed in 50% methanol with Amberlite (cation exchange resin), lost the colour of **I** which is adsorbed by the resin; thus **II** and **IV** dissociated in solution (**IV** seemed to have a molecular ratio in solution different from that in the solid). The spectra were all complex, but all the salts, tested with AgBr and AgI photographic plates, were fairly good sensitisers (remedying the weakness of **I**). The desensitising azomethin dye became a sensitiser upon coupling and the Pinacryptol Yellow after coupling remained a desensitiser but sensitised in the infra red region. C. O. C.

Trinuclear Sensitising Dyes—II. Y. Hishiki. *Repts. Sci. Research Inst.* (Japan) **28**, 405–411 (1952): *Chem. Abs.*, **47**, 11053 (10 Nov. 1953).

Lepidine ethiodide was heated with acetic anhydride at 150°C. in an oil bath and $CH(OC_2H_5)_3$ slowly dropped in. In 5–40 min. cryptocyanine was formed (determined with a Beckmann photoelectric spectrometer) largely in the beginning with no marked further increase while neocyanine was formed later in ever increasing amounts. Presumably cryptocyanine reacting with $CH(OC_2H_5)_3$ formed two intermediate products, one of which formed neocyanine by further reacting with cryptocyanine and the other gave again cryptocyanine by reacting with lepidine ethiodide. Acetic anhydride and $CH(OC_2H_5)_3$ did not form $CH_3COOCH(OC_2H_5)_2$ nor did this increase the yield of neocyanine when added specially. The distillate of neocyanine was fractionated but no pure substances could be separated. Presence of ethylacetate, acetic acid, acetic anhydride and $CH(OC_2H_5)_3$ was indicated by the b.p., a very small amount of HIO_3 was extracted by water. The amount produced was either actually small or may have linked with ethylacetate. C. O. C.

A Conductimetric Study of the Interaction of Anionic Mucopolysaccharides and Cationic Dyes. M. Schubert and A. Levine. *J. Amer. Chem. Soc.*, **75**, 5842–6 (5 Dec. 1953).

The behaviour of metachromatic and non-metachromatic dyes has been compared by measuring the electrical conductance of aqueous solutions of anionic mucopolysaccharides in presence of cationic dyes and determining the difference, Δ, between the specific conductance of a mixture of mucopolysaccharide and dye and the sum of their separate specific conductances. The results, given as values of Δ, show no evidence of a difference in binding that could serve to classify cationic dyes as either metachromatic and non-metachromatic. It could seem that the metachromatic colour is due to binding of the dye by chromotrope and not to dimerisation or polymerisation. Methylene Green and Methyl Green which have been thought to obey Beer's law and be unaffected by chromotropes, give values of Δ at least as large as those given by the metachromatic Methylene Blue and Crystal Violet which suggests that the band intensities of these dyes are not as constant as was thought. C. O. C.

Spectroscopic Nature of Chlorophyll. S. Kato, S. Tonomura, and K. Yamamoto. *J. Sci. Research Inst.* (Tokyo), **46**, 118–125 (1952): *Chem. Abs.*, **47**, 11981 (25 Nov. 1953).

The data contained in the literature, especially the data concerning the absorption and fluorescence spectra of chlorophyll-type compounds in the visible range indicate that the first strong and second weak absorption given by these compounds is attributable to the transition occurring between the vibrational excited state (one step) of the ground state and the nonvibrational state of the next higher energy level. The molecule is mostly in the vibrational excited state at room temperature because of the symmetry of the electric field caused by the hydrogenation of one of the nuclei. Fluorescence is attributable to the transition occurring between the antisymmetrical vibrational state of the ground state and the nonvibrational state of the next higher energy level. C. O. C.

The Nature of Melanin. K. Mizuno. *Kagaku* (Science), **23**, 79–80 (1953): *Chem. Abs.*, **47**, 12436 (25 Nov. 1953).

Membranes from cattle eyes were extracted with conc. H_2SO_4, filtered and the solution poured into large excess of water to precipitate melanin which was then repeatedly extracted with warm water. Extraction of the melanin

with ether gave extracts of pH 5–6 containing a yellow fluorescent substance, melanochrome, with absorption maximum at 246 mμ. Melanochrome could also be obtained by partially digesting melanin with trypsin. Melanochrome combines with congulated egg-white protein to give a black precipitate of artificial melanin. Thus the melanin is a conjugated protein (chromoprotein) consisting of melanochrome and a protein. C. O. C.

Action of Xanthopterin on Melanin Formation *in vitro*. P. Gonnard. *Ann. pharm. franc.*, **11**, 446–449 (1953): *Chem. Abs.*, **47**, 12440 (25 Nov. 1953).

Observation of the O uptake and decarboxylation of dopa (3 : 4-dihydroxyphenylalanine) in sodium acetate buffer at pH 7 by tyrosinase in presence and absence of xanthopterin shows that the latter has no influence on the first, enzymic stages, but strongly activates the last, nonenzymic, processes. The decarboxylation which accompanies polymerisation occurs before the insoluble melanins are precipitated. C. O. C.

A Selective Adsorbent for Rutin and Quercetin. M. Zâfir. *Folia Pharm.* (Istanbul), **2**, 233–5 (1953): *Chem. Abs.*, **47**, 12,751 (25 Nov. 1953).

$Bi(OH)_3$ absorbs rutin and quercetin from very dilute solutions. After converting $Bi(OH)_3$ to Bi_2S_3 the rutin can be extracted from the precipitate with alcohol acidified with acetic acid. C. O. C.

Structure of some *Fusarium* Pigments. Constitution of Solanione and Lycopersin. F. F. Nord. *Intern. Congr. Biochem., Abstrs. of Communs. 1st Congr. Cambridge, Engl.*, 243–4 (1949): *Chem. Abs.*, **47**, 11,171 (10 Nov. 1953).

Solanione, an orange-red pigment present in *Fusarium solani*, is 2-methyl-3-methoxy-6(or 7)-acetonyl-5 : 8-dihydroxy-1 : 4 naphthoquinone, the exact position of the acetonyl group being unknown. The pigment lycopersin, obtained as shiny bright red needles from a pyridine extract of *Fusarium lycopersin*, has the formula $C_{10}H_{15}O_3$. C. O. C.

Electron-microscopic Analysis of Iron Oxide Pigments. R. R. Wright and W. G. Dechant. *Virginia J. Sci.* [N.S.] **4**, 129–136 (1953): *Chem. Abs.*, **47**, 10,953 (10 Nov. 1953).

Two commercial samples of hydrated yellow iron oxide pigments were essentially identical being rod-like and approx. 0·5 μ long. Specimens for electron-microscopic examination are made by collecting 200-mesh powder on a water-borne collodion film, transferring the combination to a clean glass plate, draining excess water, and drying the film with hot-air blast. The film-forming solution is made of 35 cc. amyl acetate U.S.P. with 5 cc. collodion U.S.P. C. O. C.

Relationship between the Colour of Iron Oxide and Argillaceous Natural Pigments and their Chemical Composition. K. I. Tolstikhina. *Trudy Inst. Geol. Nauk* No. 89, *Petrograf. Ser.* No. 28, 150–9 (1948): *Chem. Abs.*, **47**, 12,831 (25 Nov. 1953).

To determine the degree of hydration of Fe in non-oxide pigments 0·05 g. samples were treated with 20 cc. of 5% HCl in the water bath for 30 min. The soln. was filtered and Fe in the filtrate determined colorimetrically. This method is based on the empirical fact that for anhydrous iron oxides the solubility in aq. HCl decreases. The data showed that the Fe in all yellow compounds is more soluble in HCl than that in red compounds. Thermal analyses were carried out in a Mars furnace at 100–900°c., a constant temperature being maintained for 2 hr. These analyses enabled the eight pigments studied to be divided into three groups: (1) clays with adsorbed iron oxide (gave the largest percentage loss on ignition at 500°c.); (2) ores contained Fe as hydration oxide (they give maximum loss of water at 300°c.); and (3) ores containing anhydrous iron oxide and adsorbed water and showing greatest loss of water at 150°c. C. O. C.

Jarositic Pigments. K. I. Tolstikhina. *Trudy Inst. Geol. Nauk* No. 89, *Petrograf Ser.* No. 28, 160–3 (1948): *Chem. Abs.*, **47**, 12,831 (25 Nov. 1953).

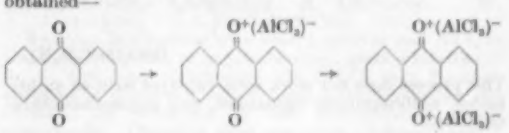
The pigments from jarositic rocks in Kazakhstan are stable to the atmosphere, and light and are useful technically. They contain S as sulphate which is not completely extracted by water and is difficult to extract with acid. However, after short calcination at 500°c. most of the S can be extracted with water. A lead jarosite after calcining at 500°c. yielded 30% SO_3 when extracted with water. Burning at 800–900°c. causes dissociation of the sulphates of the alkalimetals, lead and iron which are present. C. O. C.

A New and More Efficient Type of Leaded Zinc Oxide for Use in House Paints. C. H. Adams. *Offic. Dig. Federation Paint & Varnish Production Clubs* No. 344, 575–589 (1953): *Chem. Abs.*, **47**, 12,831 (25 Nov. 1953).

Mono-, di-, tri- and tetrabasic lead sulphates have been prepared. They contain, respectively, 50, 66·7, 75 and 80% of the Pb content in a form available for soap formation compared with only 20–25% in the commercially available basic sulphate white lead. C. O. C.

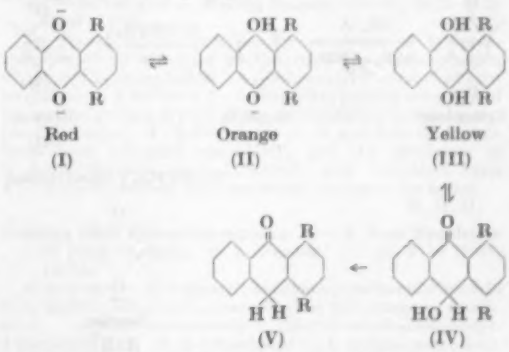
Some Chemical Problems arising in the Study of Anthraquinone Dyes. S. Coffey. *Chem. and Ind.*, 1068–1074 (10 Oct. 1953).

A brief historical survey of anthraquinone dyes and of the substitution of anthraquinone is given. Amidation of anthraquinone with hydroxylamine in sulphuric acid gives a mixture of 1-amino(17·5%), 2-amino (28·6%) anthraquinone together with a quantity of 1 : 5, 1 : 6, 1 : 7, 1 : 8, 2 : 7, diamino and polyamino anthraquinones and not 1-aminoanthraquinone as stated in the literature. Nitration of anthraquinone gives 6·6% 2-nitro 1% each of 1 : 5 and 1 : 8 dinitro and 2% each of 1 : 7 and 1 : 6 dinitro anthraquinone as well as 1-nitroanthraquinone. Anthraquinone, which is a Lewis base, forms stable acid-base complexes with, e.g. H_2SO_4, $AlCl_3$. With $AlCl_3$, 1 : 1 and 1 : 2 compounds differing in physical properties are obtained—



2-Aminoanthraquinone similarly with $AlCl_3$ gives 1 : 1, 1 : 2, 1 : 3 addition compounds.

Reduction of anthraquinone with $Na_2S_2O_4$ and NaOH gives the leuco compound (I) which on acidification goes through the following stages—



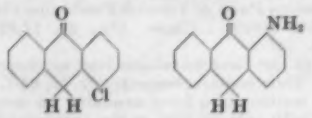
Red (I) Orange (II) Yellow (III)

Some dyes, e.g. Caledon Red 5G (R = benzoylamino), give oxanthrone compounds (IV) which are stable to mild oxidising agents and which react with the anthrahydroquinone compound (III) to give the anthrone (V) and anthraquinone.

Infrared spectra confirm the structures (VI) and (VII) given to the stable leuco compounds of 1 : 4 dihydroxy and 1 : 4-diaminoanthraquinone, which are possibly stabilised by hydrogen bonding—

(VI) (VII)

α-Substituted anthraquinone compounds give 1-substituted 9-anthrones and 4-substituted-9-anthrones depending upon the possible formation of hydrogen bonding with the carbonyl group, e.g. 1-chloro-anthraquinone → 100% 4-chloro-9-anthrone (VII) whereas 1-amino-anthraquinone gives 85% 1-amino-9-anthrone (VIII).

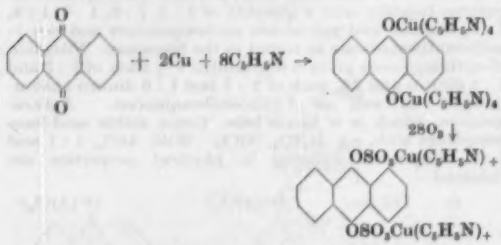


(VII) (VIII)

Similarly 5-chloro 1-amino anthraquinone gives mainly 5-chloro-1-amino anthrone.

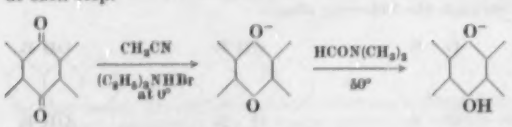
Soledon Dyes

These are the half sulphate esters of leuco vat dyes and in some cases can be obtained by reacting with alkali the copper-pyridine complexes prepared thus—

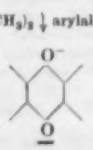


This process does not work with vat dyes such as anthrimides, anthraquinone carbazoles, and acylaminoanthraquinones.

Reduction in non aqueous media is more complex than in aqueous media as the semiquinone ⇌ quinhydrone product is stable. The reduction of anthraquinone with Zn can be carried out in such a way that the reaction can be stopped at each step.



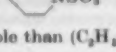
Colourless Magenta (I) Brown (II)



Scarlet (III)

Products II and III with loosely bound sulphur trioxide give Soledon dyestuffs.

Stability of sulphur trioxide–amine complexes varies, e.g. $(C_5H_5)_2NSO_3$ is much more stable than



which itself is more stable than $(C_5H_5)_2N{\cdot}COCH_2{\cdot}SO_3$.

C. H. R.

Some Anilino Compounds Related to Reductone. W. Cocker and P. Schwarz. *Chem. and Ind.*, 1126 (17 Oct. 1953).

Unlike the mono (I) and di-anilino (II where a = b = 0, X = Cl) derivatives of reductone; of which the rapid change in ultraviolet absorption spectra is caused by air oxidation of the group (III), the mesomeric salt (I where a = 1, b = 0, X = Cl) although it reduces Tillman's reagent, the change is not caused by air oxidation but as already suggested by cyclization. The blue product (I where a = b = 1, X = Br) obtained from aniline, hydrogen bromide and β-2 furylacrolein, behaves similarly. Attempts to show the presence of compounds IV and V in alkaline solutions of furfural and β-2-furylacrolein have failed.

$$PhWHCH = C(OH)CHO \quad (Ph{=}C_6H_5)$$

(I)

$$PhWH = CH(CH = CH)_aC(OH) = CH(CH = CH)_bNHPh]X^-$$

$$PhWH(CH = CH)_aCH = C(OH)(CH = CH)_bCH = \overset{+}{N}HPh]X^-$$

(II)

$$-C(OH) = C(NHR)-$$

(III)

$$HO{\cdot}CH = CH{\cdot}CH = C(OH)CHO$$

(IV)

$$HOCH = CH{\cdot}CH = C(OH)CH = CHCHO$$

(V)

C. H. R.

Reaction of Diazonium Salts with β-2-Thienylacrylic Acid. W. Freund. *J.C.S.*, 2889–2891 (Oct 1953).

Under Meerwein's conditions [cf. *J. fr. Chem.*, **152**, 237 (1939)] β-2-thienylacrylic acid and *p*-nitrobenzenediazonium chloride give only a small amount of 5-*p*-nitrophenyl-2-4′-nitrostyrylthiophen, but with other diazo-compounds the 2-styrylthiophens are obtained; β-2-furylacrylic acid generally gives the diarylated compounds. An ionic reaction mechanism appears to be favoured.

H. H. H.

Quinones. III— Addition Reactions of 1:4-Naphthaquinones substituted in the 6-Position. J. M. Lyons and R. H. Thompson. *J.C.S.*, 2910–2915 (Oct. 1953).

The products formed by addition of aniline, acetic anhydride, toluene-*p*-thiol, and bromine to 6-hydroxy-, 6-acetoxy-, 6-methyl-, 6-chloro-, and 6-acetamido-1 : 4-naphthaquinone, indicate a marked effect of the substituent on the course of the reactions, resulting in the predominant formation of one isomer in all cases except the additions of toluene-*p*-thiol. The direction of addition of aniline and acetic anhydride is in accord with the electronic character of the 6-substituent, which, however, exerts no control over the addition of toluene-*p*-thiol. Reactions with bromine are anomalous.

H. H. H.

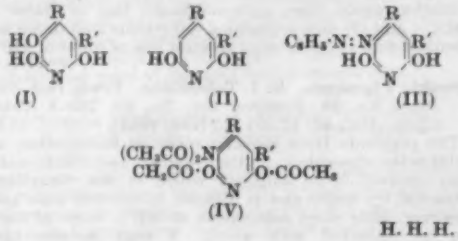
Action of some Free Radicals on Naphthalene E. Boyland and P. Sims. *J.C.S.*, 2966–2972 (Oct. 1953).

Naphthalene when oxidised with Fenton's reagent, with aqueous H_2O_2 irradiated with ultra-violet light, and with benzoyl peroxide in chlorobenzene at 80°, gives 1- and 2-naphthol or derivatives of them (according to conditions) and salicylic acid in all cases. Oxidation with H_2O_2 in ultra-violet light has also given isomeric hydroxybenzoic acids. The products were separated, after a preliminary division into acidic, phenolic, and neutral fractions, by paper chromatography.

H. H. H.

Synthesis of some Methyl-substituted 2 : 3 : 6-Trihydroxypyridines. D. E. Ames, R. E. Bowman, and T. F. Grey. *J.C.S.*, 3008–3015 (Oct. 1953).

Dihydroxypyridines (II; R = CH_3, R′ = H or CH_3) are converted, *via* the phenylazo- (III) and diacetylamino-compounds (IV), into the corresponding trihydroxypyridines (I).



(I) (II) (III)

(IV)

H. H. H.

Synthesis of 2-[8-^{14}C]-Naphthylamine. J. R. Catch, H. P. W. Huggill, and A. R. Somerville. *J.C.S.*, 3028–3030 (Oct. 1953).

2-Naphthylamine labelled with ^{14}C in position 8 is synthesised from 4-*p*-methoxyphenylbutan[^{14}C]oic acid; it has a specific activity of ~ 2·5 mc./millimole. [1-^{14}C] Naphthalene is obtained as a by-product. H. H. H.

Halogenation of β-Naphthylamine and its Derivatives. F. Bell. *J.C.S.*, 3035–3041 (Oct. 1953).

A comparison is made between the action of chlorine and of bromine on a number of 2-sulphonamidonaphthalenes. As a result, the following tentative suggestions are offered in regard to the halogenation of β-naphthylamine and its derivatives: (*a*) Entry into positions 1 and 6 represents normal attack by "molecular" halogen under the influence of the directing group in position 2. (*b*) Entry into position 3 results from attack by positive halogen or, less probably, by a halogen radical. (*c*) Entry into position 4 involves elimination of halogen halide from a previously formed additive compound. H. H. H.

The so-called "1-Fluoro-3:4-dinitrobenzene". H. Suschitzky. *J.C.S.*, 3042–3044 (Oct. 1953).

The so-called "1-fluoro-3 : 4-dinitrobenzene" (4-fluoro-1 : 2-dinitrobenzene), stated by Cannoni de Degiorgi and Zappi to result from a Balz–Schiemann reaction on 3 : 4-dinitro-aniline hydrochloride, is now shown to be 1-chloro-4-fluoro-2-nitrobenzene, the 4-nitro-group having been replaced by chlorine during the diazotisation. The true 4-fluoro-1 : 2-dinitrobenzene is obtained by nitration of *m*-fluoronitrobenzene. H. H. H.

Chemistry of the *Coprosma* Genus. VII—A Revised Constitution for Lucidin. L. H. Briggs and G. A. Nicholls. *J.C.S.*, 3068–3069 (Oct. 1953).

From infra-red spectrum data and reconsideration of known properties, the constitution of lucidin has been revised from 1 : 3 : 5-trihydroxy-2-methylanthraquinone to 1 : 3-dihydroxy-2-hydroxymethylanthraquinone. H. H. H.

Colouring Matters of the Bark of *Rhamnus alaternus*. L. H. Briggs, F. E. Jacombs, and G. A. Nicholls. *J.C.S.*, 3069–3072 (Oct. 1953).

The hydrolysed extract of this bark has yielded two colouring matters, viz. emodin (4 : 5 : 7-trihydroxy-2-methylanthraquinone) and probably the 3 : 4 : 5 : 7-tetrahydroxy-2-methyl compound, which has dyeing properties on mordanted wool and is not eluted by acetic acid from a magnesia column, both properties characteristic of vicinal dihydroxyanthraquinones. H. H. H.

Studies of Trifluoroacetic Acid. VIII—Diazotisations of Aromatic Amines in Aqueous Trifluoroacetic Acid and Other Perhalogenocarboxylic Acids. M. R. Pettit, M. Stacey, and J. C. Tatlow. *J.C.S.*, 3081–3084 (Oct. 1953).

Various aromatic amines, e.g. *p*-toluidine, mesidine, 2 : 4-dimethyl-, *p*-chloro-, and *p*-bromo-aniline, when diazotised in aq. trifluoroacetic acid with $NaNO_2$, give solid diazonium trifluoroacetates of apparent formula $R\cdot\overset{+}{N}_2\overline{O}_2\overset{\cdot}{C}\cdot CF_2CF_2\cdot COOH$. Analogous salts are given by other acids, including heptafluorobutyric (e.g. by aniline, *p*-toluidine, and *p*-chloroaniline), trichloroacetic, and perfluoro-adipic acids. In general, these salts are relatively sol. in water and in polar org. solvents, and proved to remain stable for several weeks, none of them being detonated when struck; they undergo the usual replacement and coupling reactions in aq. solution. H. H. H.

Studies in Mycological Chemistry. I—Flaviolin, a Metabolic Product of *Aspergillus citricus* (Wehmer) Mosseray. B. D. Astill and J. C. Roberts. *J.C.S.*, 3302–3307 (Oct. 1953).

The isolation of flaviolin from the mould *Aspergillus citricus* is described, and, from its general properties together with the degradation of its triacetyl deriv. to 3 : 5-dihydroxyphthalic acid, it is shown to be 2(or 3) : 5 : 7-trihydroxy-1 : 4-naphthaquinone. H. H. H.

Kinetics of the Reduction by Titanous Chloride of Nitrobenzene and its Substitution Products. S. A. Newton, jun., F. J. Stubbs, and (Sir) C. Hinshelwood. *J.C.S.*, 3384–3391 (Nov. 1953).

Reduction of nitrobenzene by $TiCl_3$ in aq. C_2H_5OH is shown to be of the first order with respect to each of these reactants and, over a certain range, inversely proportional (approx.) to the square of the hydrogen-ion concn. The active species are thought to be $C_6H_5NO_2H^+$ and a hydrolysed form of titanous ion. In the sequence $C_6H_5\cdot NO_2(1) \rightarrow C_6H_5\cdot NO(2) \rightarrow C_6H_5\cdot NH\cdot OH(3) \rightarrow C_6H_5NH_2$, (2) and (3) are reduced many times more rapidly than (1), but condensation leads to a very rapid formation of azoxybenzene, which, although it yields aniline quant., is reduced much more slowly. The diversion of a considerable part of the reaction by way of the azoxy-compound leads to a fall in bimol. constants. Substituents in the benzene nucleus have the effect expected from their electronic character. In the majority of examples, the joint effect of 2 substituents on the free energy of activation is calculable additively from their individual actions; deviations are attributed to saturation effects or to chelate interactions. H. H. H.

Oxidative Hydrolysis of 4-α-Cyanobenzyl*meso*benzanthrone. N. Campbell and A. A. Woodham. *J.C.S.*, 3429–3432 (Nov. 1953).

It is shown that 4-benzyl*meso*benzanthrone is probably an intermediate in the conversion of 4-α-cyanobenzyl-*meso*benzanthrone into 4-benzoyl*meso*benzanthrone by oxygen at room temp. in CH_3OH – KOH. The mechanism of the reaction is discussed. H. H. H.

Synthesis of Homoferreirin. K. G. Neill. *J.C.S.*, 3454–3455 (Nov. 1953).

An unambiguous synthesis of 5 : 7-dihydroxy-2′ : 4′-dimethoxy*iso*flavanone is described, which is found to be identical with the homoferreirin previously isolated from the heartwood of *Ferreirea spectabilis*. H. H. H.

Friedel–Crafts Acetylation of Chrysene. W. Carruthers. *J.C.S.*, 3486–3489 (Nov. 1953).

Reaction of chrysene with acetyl chloride and $AlCl_3$ in CS_2-acetyl chloride, or in nitrobenzene, gives a mixture of 2-, 4-, and 5-acetylchrysenes. In CH_2Cl_2 only 2-acetylchrysene is produced. 2-, 4-, and 5-ethylchrysenes are obtained on reduction of the corresponding acetyl compounds. Chrysene thus resembles phenanthrene in reacting to a considerable extent in a side ring during Friedel–Crafts acetylation in nitrobenzene or CS_2. H. H. H.

Melanin and its Precursors. VII—Synthesis of Methylated 5 : 6-Dihydroxyindoles. R. I. T. Cromartie and J. Harley-Mason. *J.C.S.*, 3525–3528 (Nov. 1953).

To obtain information on the structure of tyrosine-melanin which is formed by the oxidative polymerisation of 5 : 6-dihydroxyindole, a comparative study of the oxidation of a series of 5 : 6-dihydroxyindoles substituted by methyl groups in each of the five available positions has been envisaged. 5 : 6-Dihydroxy-1-, 2- and 3-methylindole have been prepared previously, and the syntheses of 5 : 6-dihydroxy-4- and 7-methyl- and 7-methyl- and 4 : 7-dimethylindole, now reported, complete the series. H. H. H.

Studies with Phenylbutadiene. I—A New Synthesis of Naphthalene. S. A. Faseeh. *J.C.S.*, 3708 (Nov. 1953).

A suspension of 4-phenylbutadiene-1-carboxylic acid in CCl_4 absorbs chlorine in sunlight (but not unless so irradiated), to yield successively 2 : 3-dichloro-5-phenylpent-4-enoic and 2 : 3 : 4 : 5-tetrachloro-5-phenylpentanoic acid. The former product when heated in aq. Na_2CO_3 gives 1-chloro-4-phenylbutadiene, which affords naphthalene in 82% yield when heated with vacuum-dried $SnCl_2$. This simple synthesis of naphthalene parallels that of phenanthrene from 2-formyldiphenyl. H. H. H.

Azulenes. I—A Synthesis of Azulene. D. Lloyd and F. Rowe. *J.C.S.*, 3718–3719 (Nov. 1953).

bicyclo [5 : 3 : 0] Dec-7-en-9-one when reduced with $LiAlH_4$ gives *bicyclo* [5 : 3 : 0] dec-7-en-9-ol, which when heated with $KHSO_4$ gives *bicyclo*-[5 : 3 : 0]deca-7 : 9-diene, and this compound when distilled at 1 mm. pressure in N_2 over Pd-C(20%) heated to 350°, affords deep blue needles of azulene. H. H. H.

PATENTS

***p*-Dialkylaminoaniline Developers for Phenazonium Dye Images.** General Aniline. *BP* 701,545

6-Halogeno-8-hydroxycinchoninic acids when coupled with an oxidised *p*-dialylaminoaniline containing < 3

amino groups yield azine magenta dye images in the silver halide emulsion. C. O. C.

Azo Dyes containing an Aliphatic Chain of at least 8 Carbon Atoms linked to the Diazonium Portion of the Molecule. General Aniline. *USP* 2,629,658

Azo dyes which are non-diffusing in photographic emulsions are produced by using primary amines of formula—

$$Z\cdot ANH_2\cdot(K\cdot R)_n\cdot KB$$

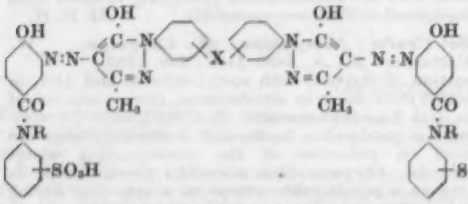
(Z = H, Alk, alkoxy, sulpho, carboxy or Hal; K = a homopolar linkage, e.g. a carbonamide linkage; A = phenyl or aminodiphenyl; B = Alk of > 7C; n = 0 or 1; R = an aromatic radical) as the diazotisable component. C. O. C.

Copper-complex Disazo Direct Cotton Blue. General Aniline. *BP* 700,701

The copper complex of the disazo compound 2-naphthol-3 : 6-disulphonic acid ← dianisidine → 3-methyl-1-*m*-sulphophenyl-5-pyrazolone is faster to light than the similar dyes of *BP* 635,621 (*J.S.D.C.*, **66**, 452 (1950)) naphtholmonosulphonic acid ← 3 : 3′-dihydroxybenzidine → a 5-pyrazolone. Its shade and light fastness are not adversely affected by application of urea-formaldehyde, etc., finishes. E. S.

Metallisable Disazo Direct Cotton Dyes. Ciba. *BP* 701,241

Disazo compounds of the type—



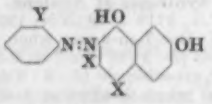
(X = direct link, –CH : CH–, –CO·NH–, or –NH·CO·NH–; R = H or Alk; further SO_3H groups may be present) are mainly orange and brown direct cotton dyes which may be metallised in substance or on the fibre. Thus (2-aminophenol-4-carboxyphenylamidesulphonic acid)$_2$ → di-phenyl-*pp*′-bis-3-methyl-5-pyrazolone dyes cotton orange-brown by the single- or two-bath aftercoppering process. E. S.

Disazo Blue-greys for Level Dyeing of Unevenly-damaged Wool. ICI. *BP* 701,442

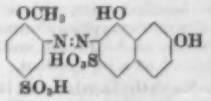
Aminoazo compounds aminosalicylic acid → *α*-naphthylamine are diazotised and coupled with *N*-mono- and dialkyl derivatives of *γ*-acid to yield blue-grey disazo dyes which are better levelling on wool which has been locally damaged (e.g. by uneven exposure to light) than the similar dyes of *BP* 287,010 derived from *γ*-acid itself or its *N*-phenyl or *N*-benzoyl derivatives. Thus the aminomonoazo compound 5-aminosalicylic acid → *α*-naphthylamine is diazotised and coupled with *NN*-dimethyl-*γ* acid under alkaline conditions. The blue-grey disazo dye so produced levels well from a neutral bath on wool which has been unevenly damaged by exposure to light. E. S.

Copperable Dis- and Poly-azo Direct Cotton Dyes. S. *BP* 700,713

Dyes which may be coppered, in substance or on the fibre, are made by coupling 1 mol. of a diazo compound with 1 mol. of a monoazo compound—



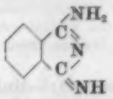
(one X = H, the other X = SO_3H; Y = a metallisable group; the benzene nucleus may contain commonly used substituents). The diazo compound may be derived from a simple amine like anthranilic acid, or from an aminomono- or dis-azo compound, or it may be the product of coupling a tetrazo compound with 1 mol. of a naphthol. Thus tetrazotised *o*-dianisidine is coupled with an alkaline soln. of 1-naphthol-3 : 8-disulphonic acid and the product further coupled in aq. pyridine with the monoazo compound—



to yield a navy blue dye for cellulosic fibres whose fastness is improved by aftertreatment with Cu salts. E. S.

Phthalocyanine Intermediates and their Use in producing Phthalocyanines on the Fibre. FBy. *BP* 698,049

1-Amino-3-imino*iso*indolenine



and its *N*-alkyl, *N*-aryl or *N*-acyl derivatives are intermediates which may be converted on the fibre to a phthalocyanine. They are made by carrying out a synthesis similar to that of a phthalocyanine, without a metal salt, and with or without a substance capable of supplying an anion stable at the reaction temperature, e.g. a nitrate. Alternatively the complex obtained by carrying out a modified phthalocyanine synthesis in presence of a copper salt is treated with nitric acid; or an *o*-arylene dinitrile is heated at ca. 100°C. in an alcohol containing an alkali metal alcoholate, with ammonia, an amine, or a compound capable of yielding ammonia, e.g. sodamide. Thus, phthalic anhydride is heated at 150–160°C. for 20 hr. with urea and ammonium nitrate containing a small amount of ammonium molybdate.

BP 698,070

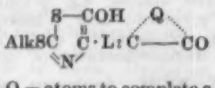
The corresponding 1-alkoxy derivatives, which are also suitable for converting to phthalocyanines, are made by treating an *o*-arylene dinitrile with an alkali metal alcoholate in an alcohol. Thus phthalonitrile is stirred at 35–40°C. with a solution of sodium in methanol. The resulting 1-methoxy-3-imino-*iso*indolenine is separated by cooling to − 10°C.

BP 698,039

The compounds described above are used for printing textiles by incorporating them in a printing paste along with a compound of a metal, e.g. copper, capable of forming phthalocyanines, and a water-miscible solvent, e.g. a mixture of formamide and ethylene glycol. R. K. F.

Oxonol Dyes. Kodak. *BP* 702,247

Dyes of formula—



(L = polymethin; Q = atoms to complete a 5 or 6 membered heterocyclic ring) particularly those where Q = atoms to complete a 2-alkylthio-5-thiazolone nucleus) have sensitising power approaching that of merocyanine dyes. C. O. C.

Water-dispersible Dye Powders. General Aniline. *BP* 701,814

The powdered dye is attrited by gaseous fluid energy of such intensity that the average particle size is reduced to < 15 *μ*, preferably 10 *μ* with a maximum of 60 *μ*, preferably 15 *μ*. A finely ground dry solid dispersing agent is mixed in at any stage of the process. The product yields aqueous dispersions of equal or better quality compared with those obtained by plastic milling. C. O. C.

Tanning Agents, Dye Intermediates, Agents for Reserving Wool, etc. (III p. 127).
Association of Dye Ions in Aqueous Solutions (VIII p. 134).
Investigations on Colour Development. VII—Action of Atmospheric Oxygen on Developers containing Sulphite and Coupler. VIII—Mechanism of the Air Oxidation of Developers containing Couplers (IX p. 135).
Antihalation Dyes (IX p. 135).

V—PAINTS; ENAMELS; INKS

Measurement of the Brightness of White and Black Coatings. C. F. Spiess and W. Eisner. *Farbe u. Lack.*, **59**, 320–3 (1953): *Chem. Abs.*, **47**, 11,756 (10 Nov. 1953).

The light reflectance at 45° with MgO = 98% as standard, was 97% for blanc fixe, 90% for Sachtolith (ZnS), 96% for TiO_2 and 95% for Zinc White WS. Lacquers containing 15% white pigment sprayed on white sheet steel gave reflectance values which depended upon the film-thickness; in thin films (15 μ) the reflectance was also affected by the hiding power of the pigments. Film thickness had less effect on the reflectance of lacquers containing the strongly hiding TiO_2 and ZnS than it had on lacquers containing lithopones or ZincWhite. The reflectance of TiO_2 and ZnS lacquers reached a maximum at 30% pigment content; a lacquer with 30% TiO_2 maintained a reflectance of 89% down to 65 μ and of 84% down to 35 μ film thickness. The diffuse reflectance was lower for glossy films than for matt films and both gave lower values than the pigments themselves. Black coatings also showed decreasing reflectance with increasing gloss values; thus, baking conditions strongly affect the depth of colour of black coatings. C. O. C.

More Production from your Present Pigment-dispersion Equipment. R. B. Shurts. *Natl. Paint, Varnish, Lacquer Assoc., Sci. Sect.*, Circ. No. **753**, 244–261 (1951): *Chem. Abs.*, **47**, 12,831 (25 Nov. 1953).

A review of production problems and a discussion of ways to increase production of satisfactory paints using existing equipment. Among factors considered are fineness of grind in relation to texture, opacity and tinting strength, non-settling and flooding or floating of certain pigments, water resistance of film and final durability, and its effect on gloss and gloss retention. C. O. C.

PATENT

Alkyl Aryl Sulphonate—Liquid Hydrocarbon—Aliphatic Hydroxy Compound Compositions—Printing Inks, Paints and Dry Cleaning Agents. Wyandotte Chemicals Corpn. *USP* 2,629,697

A base product of use in formulating printing inks, paints, and liquid dry cleaning compositions where it is desired to obtain the advantages of a wetting agent, e.g. Na kerylbenzenesulphonate, in presence of a liquid hydrocarbon is produced by adding an aliphatic hydroxy compound to a mixture of kerosene (6 parts by wt.), sodium kerylbenzenesulphonate (1–2). With addition of as little as 2% by wt. of the hydroxy compound the mixture becomes very fluid and transparent or translucent. C. O. C.

Polymeric Polyacids—Auxiliary Agents, etc. (III p. 126).

VI—FIBRES; YARNS; FABRICS

The Interpretation of Infrared Dichroism in Fibrous Protein Structures. R. D. B. Fraser. *J. Chem. Phys.*, **21**, 1511–1515 (1953): *Chem. Abs.*, **47**, 11,829 (25 Nov. 1953).

Increasing use of infrared dichroism measurements in studying the molecular structure of fibrous proteins necessitates critical examination of its interpretation. Relations between transition moment direction and dichroic ratio are derived for perfectly and imperfectly oriented fibres and the effects of reflection losses, form dichroism and convergence are considered. Uncertainties in the assignment of the transition moment directions associated with the principal vibrations of the CO·NH group are discussed. C. O. C.

Effect of Bromine on Superpolyamides. H. vom Hove. *Naturwissenschaften*, **40**, 200 (1953): *Chem. Abs.*, **47**, 12,822 (25 Nov. 1953).

Bromine reacts with polyamides causing them to dissolve; in absence of water they do not disintegrate. Per mol. unit of polyamide 6·5–15 Br atoms are consumed. Probably the Br surrounds the H of the acid amide group. With increasing molecular size in a polymer homologue series more Br per unit is used, evidently the available energy of the H increases in the series. Determination of the Br binding capacity of polyamides is believed to be important for their classification. C. O. C.

PATENTS

Pigmented Viscose Rayon. Courtaulds. *BP* 701,448

Two mercury pumps supply "dye viscose" (i.e. viscose containing a large amount of a colouring matter) and ordinary viscose respectively in a constant ratio to the spinning machine. There is a power coupling between the two metering pumps and either a hydraulic accumulator or a slip clutch to keep the rate of supply of the mixed viscoses to the spinning machine equal to the demand. C. O. C.

Fibres from Casein or other Protein of Similar Properties. Courtaulds. *BP* 701,645

Modification of *BP* 614,500, the number of necessary steps following hardening being reduced. A solution of the casein is extruded into a coagulant and the freshly-formed fibres treated with an aq. soln. containing an ionogenic compound giving rise to cyanic ions so that the heated fibres contain or carry no free chemically uncombined cyanate followed by drying at 50–90°c. C. O. C.

Polyamides of Improved Affinity for Dyes. DuP. *USP* 2,630,423

The products obtained by condensing with liberation of CO_2 the *N*-carbonanhydrides of hydrocarbon monocarboxylic esters of α-monoprimaryaminocarboxylic acids which are hydrocarbon except for the amino and carboxy groups and one alcoholic hydroxyl group situated on carbon separated from the carboxyl by a saturated aliphatic chain, have good fibre-forming properties. They have better dyeing properties and more response to aqueous treatments than the hitherto available polyamides. C. O. C.

Nylon Sewing Thread of Low Extensibility. British Nylon Spinners. *BP* 701,202

Stretching nylon thread and depositing nylon on it while it is stretched markedly reduced the extensibility of the thread and so reduced its tendency to pucker the cloth being sewn and to break when sewing at high speed. C. O. C.

Homogeneous Solutions of Acrylonitrile Polymers or Copolymers. Vereinigte Glanzstoff-Fabriken. *BP* 701,469

Homogeneous solutions which can be spun without variations in titer or thread breakage are obtained by grinding the polymer or copolymer so that it passes a screen of 2000, preferably 4000, meshes per sq. cm., and dispersing the ground product at room temperature in a solvent in a kneading machine, adding the polymer in portions with constant stirring over a considerable period, e.g. 90–120 min. Finally the dispersion is kneaded with gradual heating to 55°c, followed by gradual heating, e.g. for 2–3 hr., to 60–70°c.

BP 702,248

Modification of *BP* 698,714, particularly good spinning solutions being obtained if the solvents contain < 1%, preferably < 0·2% water. C. O. C.

Polyacrylonitrile Solutions. P. Halbig. *BP* 701,652

Polymers and copolymers of acrylonitrile in finely powdered form readily dissolve at room temperature in nitric acid of 54% by weight strength or more. If acid below this strength is used then a readily flowing mixture but not a solution is produced, heating however results in a solution being formed. C. O. C.

Dyeable Polyacrylonitrile Fibres. Chemstrand Corpn. *BP* 701,475

Non-dyeable acrylonitrile polymers and copolymers are given affinity for dyes by incorporation of substantial amounts of polymers of *N*-vinylimidazole. C. O. C.

Acrylic Copolymers having Affinity for Acid Dyes. American Cyanamid Co. *BP* 702,017

Copolymers of acrylonitrile and 1–10% of a dialkyl aminopropylacrylamide of formula—

$$CH_2 = CHCONH(CH_2)_3R^1R^2$$

(R^1 and R^2 = Alk) e.g. *N*-(3-dimethylaminopropyl) acrylamide are useful for spinning into fibres having affinity for acid dyes. W. G. C.

Stretching Polythiourea Fibres. Courtaulds. *BP* 701,806

The strength and heat resistance of polythiourea fibres are improved by stretching the pre-formed fibres > 450% in a hot swelling agent, e.g. water, so that the extensibility

of the stretched fibres is 15–25%, and then annealing the fibres without allowing them to contract. W. G. C.

Chemical Transformations in Cellulose under the Action of Hypochlorite (VII below).

VII— DESIZING; SCOURING; CARBONISING; BLEACHING

Chemical Transformations in Cellulose under the Action of Hypochlorite. E. D. Stakheeva-Kavezneva, V. I. Ivanov, and A. S. Salova. *Bumazh. Prom.*, **28** (7), 6–11 (1953): *Chem. Abs.*, **47**, 12,799 (25 Nov. 1953).

Purified cotton cellulose was treated "at 5% consistency" and 19°c. for 22 hr. with aq. NaOCl (3·5 g./l. active Cl). The proportions of COOH, CHO, CO, carbonate ester and hydroxy ketone groups were (%) 0·13, 0·16, 0·07, 0·047 and 0·045 for oxidation at pH 5; 0·36, 0·16, 0·13, 0·016 and 0·047 at pH 7 and 0·23, 0·05, 0·09, 0·00 and 0·009 at pH 10·5. For oxidation at pH 4·6, 7·0 and 10·5 the O requirements in equivalent/100 glucose units were 12·4, 16·2 and 7·4; the groups oxidised/100 glucose units 2·80, 4·46 and 3·26; viscosity ratios of cellulose nitrate solutions prepared from the oxidised cellulose were 0·221, 0·228 and 0·247; of cuprammonium solutions 0·135, 0·149 and 0·214; % α-cellulose 73·3, 71·3 and 90·1; and the yield 94·7, 92·3 and 96·1% respectively. NaOCl oxidation in acid or neutral medium involves two basic reactions: the oxidation of primary CH_2OH groups to CHO, some of which are further oxidised to COOH, and formation of α-hydroxyketone groups, which are further oxidised with rupture of the pyran ring and formation of carbonate esters. Some of the COOH groups are in lactone form. In alkaline medium the CHO groups from the primary OH groups are almost all converted to COOH; monoketones are formed and isomerised to enediols which rapidly undergo ring rupture with formation of two monuronic COOH groups; no carbonate esters are present. The CHO, hydroxyketone and carbonate ester groups in cellulose oxidised in acid or neutral medium decrease its stability in alkaline media; this accounts for the decreased cuprammonium viscosity and α-cellulose of cellulose oxidised in acid and neutral medium. The yield of cellulose in oxidation is a function of the degree as well as the type of oxidation, e.g. at O consumption of 16 equivalents/100 glucose units the approx. yield is 96·5, 95 and 92·5% for oxidation at pH 10·3, 4·6 and 7 respectively and at 24 equivalents/glucose unit 94·5, 92 and 87·5 for pH 10·3, 4·6 and 7. C. O. C.

PATENTS

Bleaching Cellulose. Chicopee Manufacturing Co. *BP* 702,300

A bleaching process particularly applicable to grey cotton consists in impregnating the fibres with a solution of a per compound which is kept inactive until the fibres are thoroughly impregnated, and then activating the solution. C. O. C.

Scouring Raw Wool. U.S. Secretary of Agriculture. *USP* 2,629,723

The wool is extracted with an aqueous liquor containing an emulsifying agent, a polar, neutral, oxygenated organic compound, e.g. butanol, and, preferably, also a neutral inorganic electrolyte. The spent liquor is regenerated by adding more of the polar organic compound, sufficient to separate the wool grease from the solution. C. O. C.

VIII— DYEING

Association of Dye Ions in Aqueous Solutions. H. Vedaira. *Bussoiron Kenkyu*, No. **65**, 58–64 (1953): *Chem. Abs.*, **47**, 11,908 (25 Nov. 1953).

The free energy of an aqueous solution of dye is calculated by a crude lattice model. Assuming association equilibrium between dye-anion micelles and the mono dispersed dye anions, then the micelles grow with increase in concentration of the dye or of added salts and the size of a micelle is influenced by the number of conjugated double bonds, ionised radicals and lyophilic radicals of the dye anions. C. O. C.

Effect of Copper in Wool Dyeing. L. F. Story. *Textile Mnfr.*, **79**, 654–5 (Dec. 1953).

Use of copper sulphate in sheep dips is on the increase, resulting in copper-contaminated wool. This contamination is usually of the order of 10–15 p.p.m. but even this small amount is able to interfere with pastel dyeings even in presence of copper-sequestering agents, e.g. ethylene diaminetetraacetic acid, unless there is a large excess (8–10 mol. per atom of copper) of the latter. C. O. C.

The Dyeing of Nylon with Binary Mixtures of Acid Dyes. J. A. Albert. *Ing. textil* (Barcelona), **20**, 114–124 (1953): *Chem. Abs.*, **47**, 11,739 (10 Nov. 1953).

Five 2 g. samples of nylon cloth, each put in a wire basket after folding once (to present one unobstructed surface), were dyed in five baths (100 mol. each) kept at 85°c. in a Marney machine, for 45 min., washed in cold water and oven dried at 50°c. The dyebaths contained 0·25, 0·5, 1·0, 2·0 and 4·0% each of Lissamine Fast Yellow 2GS and Lissamine Sky Blue R8 in distilled water and 6% of 85% formic acid. The same baths, to which a further 6 ml. of 85% formic acid were again added, were then re-used to dye fresh pieces of nylon cloth for 30 min. to determine the exhaustion of the baths. Pairs of the cloth dyed in the fresh and used baths were mounted, superimposed, and photographed through yellow, blue and red filters. The first series (fresh baths) went from green (0·5% total dye) through bluish green (2%) to blue, while the second series (used baths) went from colourless (0·25%) to ivory (1%), yellow (2%), greenish yellow (4%), and bluish green (8%). This shows that both dyes were exhausted from 0·5 and 1·0% solution, and then there was preferential exhaustion of the blue until no yellow dye is taken up above a dye conc. of 2·0%. C. O. C.

PATENTS

Thiourea Dioxide for Reducing Vat Dyes. Hardman & Holden. *BP* 702,040

More stable vats are obtained if reduction is carried out with thiourea dioxide instead of sodium hydrosulphite or sodium sulphoxylate formaldehyde. Excess thiourea dioxide should be used, the excess remains stable in the solution after acidification and so enables the acid leuco vat to be used in printing pastes. After reduction and acidification the vat can be used for colouring protein or polyamide materials or for mixtures of them with cellulosic fibres although the latter show much less affinity for the acid vat.

BP 702,041

At 100°c. vat dyes can be reduced by thiourea dioxide under neutral or acid conditions. This enables protein or polyamide materials to be treated with a mixture of an indigoid, thioindigoid or naphthoquinoneindigoid vat dye and thiourea dioxide, treated at 100°c., e.g. in an ager, and the leuco dye then oxidised.

BP 702,050

An acid leuco vat dye is impregnated into cellulosic material and then oxidised in the usual manner. When reducing with thiourea dioxide under neutral or acid conditions and under conditions of high humidity, preferably in presence of liquid water, temperatures as low as 80°c. can be used.

BP 702,056

The above process is also applicable to cellulose acetate if a swelling agent is present.

BP 702,075

Preformed dispersions of acid leuco vat dyes prepared by alkaline reduction of a vat dye with thiourea dioxide and subsequent acidification are used for colouring cellulose acetate. C. O. C.

Dyeing Polyamides or Polyurethans. Basf. *BP* 701,192

Level dyeing with very good exhaustion is obtained by dyeing with complex metal compounds of azo dyes or azomethin dyes free of SO_3H groups in presence of water-soluble polyhydroxyalkyl ethers, e.g. ethylene oxide–higher fatty acid condensates, and causing the pH value of the bath to decrease during dyeing. C. O. C.

Colouring Polyester Fibres, Films, etc. ICI. *BP* 701,968

Fast colourations are obtained by padding or printing with an aqueous solution or dispersion of a dye and then fixed by steaming under superatmospheric pressure.

BP 702,328

Terylene is coloured satisfactorily by applying a dye to it, drying and heating while holding it under tension to prevent shrinkage. Textiles so treated require no separate setting. C. O. C.

Garment Dyeing and Finishing. Etablissements A. Emery & Co. *BP* 702,434

The garments are placed on forms in a vat having an air-tight locking device, and are treated in the vat successively with the necessary liquors. The garments are dried either in the vat or outside it before being removed from the forms. C. O. C.

Improving the Fastness to Wet Processing and Light of Direct Dyes (III p. 127).

IX— PRINTING

Investigations on Colour Development. VII— Action of Atmospheric Oxygen on Developers containing Sulphite and Coupler. VIII— Mechanism of the Air Oxidation of Developers containing Couplers. W. Brune and U. Kronacher. *Z. wiss. Phot.*, **48**, 1–15 (1953): *Chem. Abs.*, **47**, 12,065–6 (25 Nov. 1953).

VII— To investigate the oxygen oxidation of *NN*-diethyl-*p*-phenylene diamine (I) in presence of Na_2SO_3 and 1-phenyl-3-methyl-5-pyrazolone (II) three developing solutions were made with a I : sulphite ratio of 1 : 1, 1 : 2 and 1 : 3; similar solutions containing also 1 mg. Cu^{++}/l. were also made; all the solutions contained 50 g. K_2CO_3/l. and as much II as I. In absence of Cu, the ratio of I : sulphite consumed was 1 : 1·3 to 1 : 1·6 during the first few hours but the ratio increased to approach 1 : 2 when the reaction was allowed to go on long enough. Presence of Cu did not greatly increase the rate of oxidation but decreased the ratio of I : sulphite consumed. When NH_2OH was added in molecular concentration equal to that of the Na_2SO_3 (in absence of Cu) no change in I occurred during the first few hours but the rate of consumption of sulphite increased.

VIII— Oxidation of I by O yields benzoquinone di-imide (III) and H_2O_2; H_2O_2 reacts with sulphite to give sulphate and with I to form a peroxide which, on contact with sulphite, gives sulphate and III. III reacts with sulphite to give sulphonate and with the coupler to give a leuco base which can be oxidised to dye with H_2O_2. Analysis of solutions made from I, Na_2SO_3 and II in the ratio 1 : 2 : 1 showed that, after partial oxidation, 1–2 mol. of sulphite are used per mol. of I oxidised. The sulphate formed is equivalent to about half of the sulphite consumed. C. O. C.

Antihalation Dyes. J. Tsuno. *Konishiroku Rev.*, **3**, 1–41 (1952): *Chem. Abs.*, **47**, 12,065 (25 Nov. 1953).

Review, 50 references. C. O. C.

PATENTS

Pigmented Prints and Coatings on Fibrous Material. Basf. *BP* 701,139

In printing with resinous precondensates excellent fastness of the prints to water and rubbing is obtained by using as binding agents aqueous solutions or dispersions of mixtures of organic polymers containing reactive H atoms with precondensates of thermosetting products and reacting the reactive groups of the binding agent with nitrogenous cross linking agents which form addition products with the binding agent when heated. C. O. C.

Dye Transfers. F. J. Pitt. *USP* 2,629,647

When a compressible fluid absorbent material, e.g. unbleached muslin, is impregnated with less of an aqueous dye solution than gives complete saturation at normal temperatures and pressures, the impregnated material may be used to transfer the dye to other textiles or paper by placing them together and then compressing them. Transfer of the dye is much facilitated if the textile or paper to which it is to be applied is previously wet out. Ornamental effects may be obtained by use of transfers of different shapes and/or colours. C. O. C.

Screen Printing on Flat or Slightly Dished Circular Surfaces. L. G. Dubuit. *BP* 702,402

Dry Developed Diazotype Materials. Ozalid Co. *BP* 702,294

Paper or other base is coated with a water-insoluble gas-permeable diazotype lacquer capable of dry development. The lacquer is made from an aqueous emulsion of a polymerisable vinyl compound which has been polymerised to the stage where the emulsion droplets are still liquid. The emulsion is stabilised to electrolytic precipitation and has the property of breaking during drying to give a continuous film which when heated polymerises further to give a water-insoluble lacquer permeable to ammonia vapour. This emulsion is mixed with an aqueous solution containing a light-sensitive diazo compound, a coupling component and a fixed acid. C. O. C.

Multicolour Negative Film with Integral Masking Images. General Aniline. *USP* 2,629,657

The masks are produced within the individual layers of the colour negative thus obviating any difficulties of registration. C. O. C.

Avoiding Colour Developer Stain when forming Azine Dye Images. General Aniline. *BP* 710,341

An azine multilayer colour film is rinsed after colour development with an aq. soln. containing 0·1–10·0% each (by wt.) of formaldehyde and a water-soluble acid. Presence of formaldehyde prevents the acid forming an insoluble complex with the residual 2 : 4-diaminoaniline developing agent, while presence of the acid promotes formation of a 2 : 4-diaminoaniline-formaldehyde complex which is readily removed by rinsing in water. C. O. C.

Fusion Photothermography. Eastman Kodak Co. *USP* 2,629,671

A base sheet which absorbs radiant heat incorporates a uniformly distributed layer of ink in a vehicle of m.p. 20–200°c. When the sheet has been heated to just below its m.p. a two-tone heat image is applied by radiation of sufficient intensity and duration to raise the hot tone areas above the m.p. and so melt the ink vehicle in those areas, that in the other areas remaining unaffected. C. O. C.

Tricolour Separations in Colour Photography. General Aniline. *BP* 701,551

A method of preparing tricolour separations of the individual colour record from multilayer material in which the individual layers are sensitive to different regions of the spectrum and are in contact with each other during exposure. C. O. C.

High Speed, Colour Photographic Silver Dye Bleach-out Materials. General Aniline. *BP* 701,843

A high speed multilayer material suitable either for use in the camera or for prints contains in the yellow and magenta image layers colourless non-diffusing azo dye couplers which react with one and the same diazonium salt to form yellow and magenta dyes. The cyan layer contains a colourless heterocyclic nitrogenous compound capable of being bleached by a silver dye bleaching bath and which reacts with a metal salt to form a cyan metal complex. C. O. C.

Mixed-grain Colour Photography. Kodak. *BP* 702,200

Aminothia-2′-cyanines and their Sensitising Properties (IV p. 127).

p-Dialkylaminoaniline Developers for Phenazonium Dye Images (IV p. 131).

Thiourea Dioxide for Reducing Vat Dyes (VIII p. 134).

Colouring Polyester Fibres, Films, etc. (VIII p. 134).

X— SIZING AND FINISHING

Action of Hexamethylene Di*iso*cyanate on Benzene-containing Regenerated Cellulose. H. Krässig. *Makromol. Chem.*, **10**, 1–21 (1953): *Chem. Abs.*, **47**, 12,822 (25 Nov. 1953).

Regenerated cellulose fibres were treated with hexamethylene di*iso*cyanate after the water in the cellulose had been displaced by benzene. This gave a cellulose containing approx. 3·5% N corresponding to the ratio 4 mol. cellulose 1 mol. benzene. The swelling of the cellulose decreased by approx. 50%, it was insoluble in cuprammonium and its diurethane bonds resisted washing. By reacting either the benzene-treated material with 85% HCOOH or the $KHSO_4$-degraded samples with 10% NaOH, it was shown that the hexamethylene di*iso*cyanate had reacted with the cellulose, thus forming the diurethane bonds. C. O. C.

PATENTS

Dimensional Stabilisation of Tubular Fabrics. Samcoe Holding Corpn. *BP* 701,792

The fabric before or after being relaxed longitudinally is treated with steam or sprayed with water and is then dried by air or cylinders without any longitudinal tension being imparted to it.

BP 701,793

The fabric is steamed while relaxed longitudinally and is immediately rolled on a mandrel without any intermediate treatment. The fabric is fed into the machine by a propeller which spreads the fabric to the desired width while compressing it longitudinally.

BP 701,836

The propeller comprises a frame to be inserted within the fabric and two sets of endless belts supported on and one at each end of the frame. The belts at one end of the frame are driven faster than those at the other end. C. O. C.

Stabilising Paper, Fabrics, etc. made from Cellulose against Dimensional Change caused by Variation in Humidity of its Surroundings. Upson Co.

USP 2,629,674

Impregnation with a polyhydric alcohol, if desired together with a resin, renders cellulose immune to dimensional change when the humidity of the surrounding atmosphere is changed.

USP 2,629,701

Components containing > 1 OH group at least one of which is part of a carboxyl group, e.g. monoethylene glycol monophthalate, are used. C. O. C.

Finishing Terry Fabrics. Cannon Mills Co.

USP 2,629,918

The natural resiliency of the pile of terry fabrics is restored, e.g. after bleaching, by passing the wet fabric under tension over vibrating rollers the first of which rotate in the same direction as the fabric and the last of which rotate in the opposite direction to that of the fabric. C. O. C.

Reducing the Felting Power of Wool. Courtaulds.

BP 702,339

The process described in *BP* 701,645 when applied to fabrics containing wool reduces the shrinkage of such fabrics during scouring and milling. The fabric is impregnated with 2–4% of its weight of a metal cyanate from aqueous solution and dried at 50–90°C. C. O. C.

Continuous Setting of Wool Fabrics. Pacific Mills.

BP 701,729

The fabric in open width is impregnated with an aqueous solution of pH 9–12 and then, while kept taut in both warp and weft and kept flat and moving, is heated so as to generate steam in it for 14–21 sec., generation of steam being stopped while the fabric contains > 20% of its weight of the liquor. The set so produced resists boiling for at least 1 hr. C. O. C.

Elastic Fabrics. United States Rubber Co.

BP 702,515

Modification of *BP* 648,644. In cases where the heat-shrinkable filaments are not destroyed or rendered inactive by heat alone they can be rendered inactive by stretching the fabric in the direction in which these filaments extend and then, while stretched, heating it to considerably above 100°C. This causes the filaments to break into very short lengths so that they no longer interfere with the stretching of the fabric. C. O. C.

Rendering Fabrics containing Synthetic Hydrophobic Fibres Less Liable to Entrain and Hold Moisture. Joseph Bancroft & Sons Co. *BP* 700,755

Fabrics containing synthetic hydrophobic fibres of m.p. > 400°F., are rendered much less liable to entrain or retain moisture (and therefore to dry more quickly) by impregnating them with a resinous precondensate, drying, and either calendering under 250–3000 lb. per lineal inch of bowl pressure or pressing under 100–3000 lb. per sq. in. pressure, the calender or press being heated so that the precondensate is cured. The finished fabric should contain 0·5–15% on its dry weight of the resin. C. O. C.

Heat Setting of Nylon and other Thermoplastic Fabrics. Palatine Dyeing Co. *USP* 2,629,162

The fabric is carried on a pin tenter through a chamber containing hot metal plates placed parallel to and a few inches below and above the fabric. The peak of the radiation emission of the plates at the temperature used should coincide with the highest wave-length band for the fabric being treated. In the case of nylon temperatures of 600–900°F. are used. C. O. C.

Applying Foamed Rubber Latex to Carpets, etc. V. Golden. *BP* 2,629,919

The back of the carpet is treated with an anti-foaming agent, e.g. tributylphosphate or pine oil, and then with a rubber latex which has been whipped into foam. Finally it is dried and cured for 30 min. at 250°F. C. O. C.

XI—PAPER AND OTHER CELLULOSIC PRODUCTS

Conversion of Cellulose I to Cellulose III by Ethylamine. J. Mann and H. J. Marrinan, *Chem. and Ind.*, 1092 (10 Oct. 1953).

Treatment of bacterial cellulose with ethylamine and then extracting immediately with chloroform gives a lowering of crystallinity and a sharp absorption band at 3484 cm.$^{-1}$ due to the formation of Cellulose III. This has been confirmed by X-ray diffraction. If instead of extracting with chloroform, the ethylamine is allowed to evaporate, only a reduction in crystallinity is obtained. C. H. R.

PATENTS

High-glaze Waxed Paper or Cardboard. N. V. de Bataafsche Petroleum Maatschappij. *BP* 701,360

Paper or cardboard coated or impregnated with macro- and/or microcrystalline paraffin wax, and having a temperature of about or above the melting point of the wax is glazed by cooling rapidly by passing it through mercury at > 30°C. S. V. S.

Carbon Paper. Firma W. Koreska. *BP* 701,439

One side of a light coloured paper is coated with a solution of polystyrene, e.g. in trichlorethylene, which may contain a pigment, to form a thin coloured layer of polystyrene, and the other side is treated with carbon ink. The pigment may be applied before or after the polystyrene solution, and the uncarboned side of the paper may be coated with a light layer of wax before the polystyrene solution is applied. The finished paper does not tend to curl with variations in atmospheric conditions. S. V. S.

Transfer Copying or Manifolding Materials. W. H. Smith & Son. *BP* 702,063

A transfer copying assembly comprises superimposed flexible sheets having proximate surfaces, or a flexible manifolding sheet has opposite surfaces, with adherent, non-tacky coatings of a light-coloured metallic salt (not a sulphide) and a light-coloured water-soluble metal sulphide respectively, which, when forced into intimate contact with one another, produce a dark coloured product. The coatings are applied as emulsions containing a volatile organic liquid and a small amount of water and then dried. S. V. S.

Stabilising Paper, Fabrics, etc. made from Cellulose against Dimensional Change caused by Variation in Humidity of its Surroundings (X this page).

XIII—RUBBER; RESINS; PLASTICS

Degradation of Natural Rubber in Solution *in Vacuo*. W. F. Watson. *Inst. Rubber Ind. Trans.*, **29**, 202–214 (1953).

Rubber in solution becomes degraded in absence of oxygen and this non-oxidative degradation is the main cause of the decrease in viscosity of rubber solutions in storage. The rate of degradation is proportional to the rubber concentration and is independent of the initial purity and mol. wt. of the rubber. It is not influenced by various non-polar rubber solvents but is accelerated by acids. This phenomenon is probably associated with the gelling of solid rubber in storage. C. O. C.

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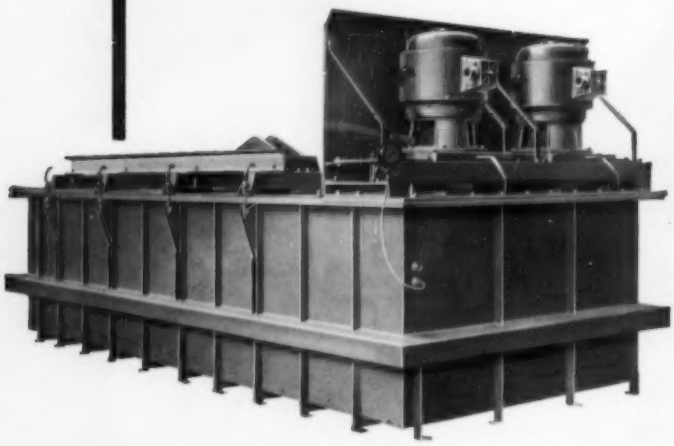

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Replies may be addressed "Box —, Society of Dyers and Colourists," Dean House, 19 Piccadilly, Bradford 1, Yorks., where all communications relating to these Advertisements, which are treated in strict confidence, should be addressed.

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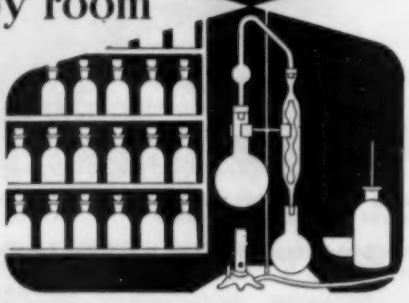

Standards, like prices, have gone up since 1869, when the first issue of Nature reproduced an address presented by the Rev. W. Tuckwell to the British Association Meeting in Exeter containing the above passage.
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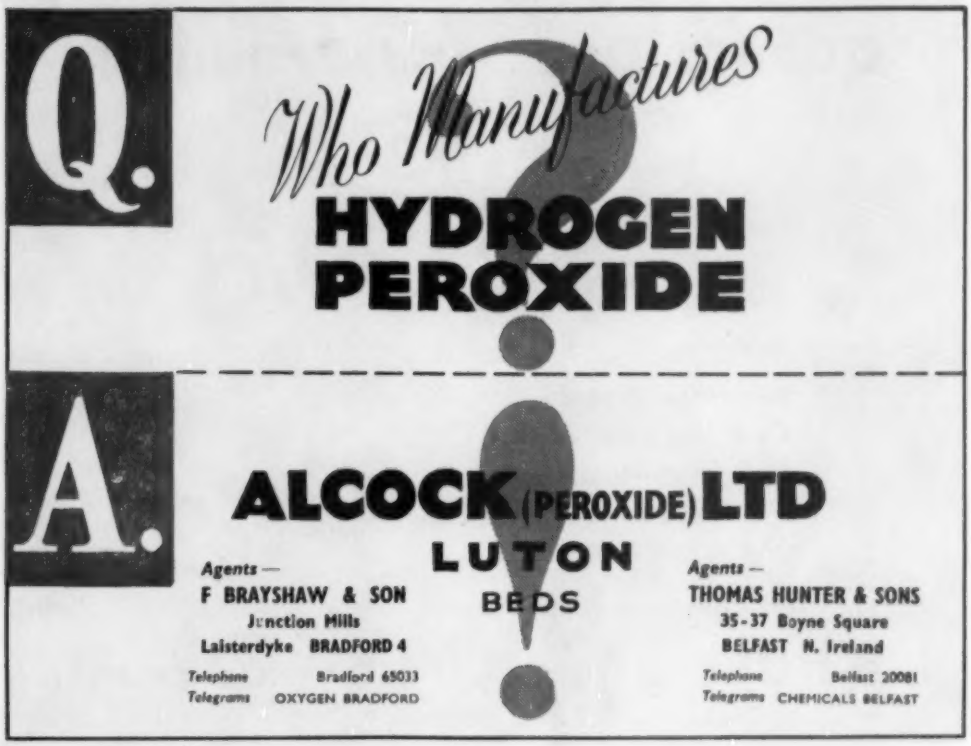
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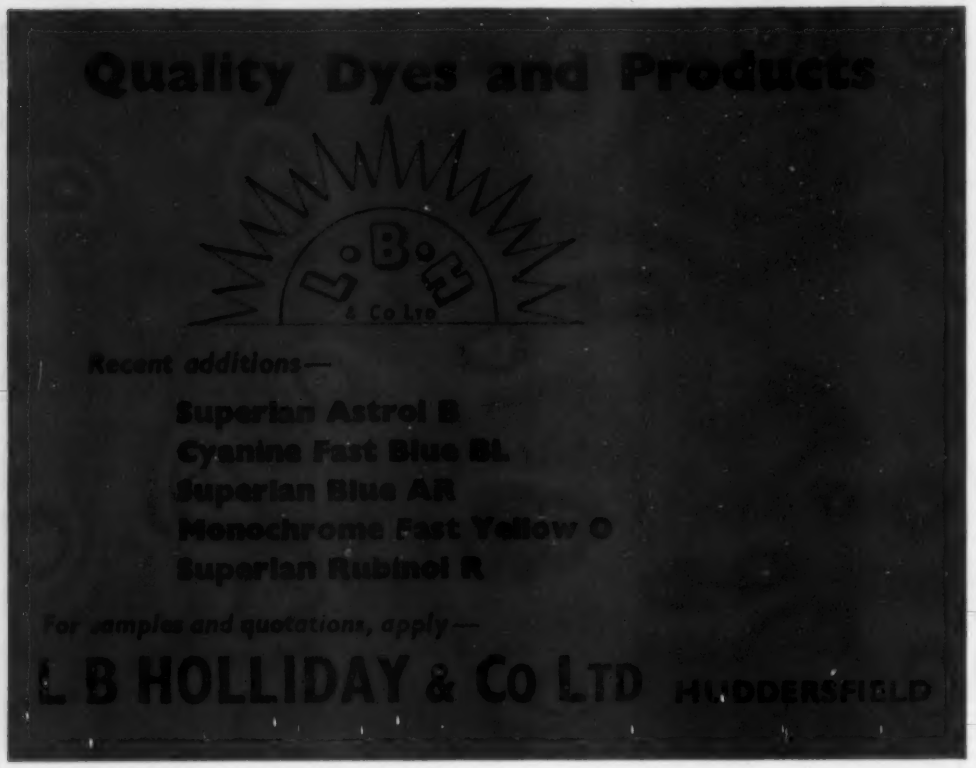
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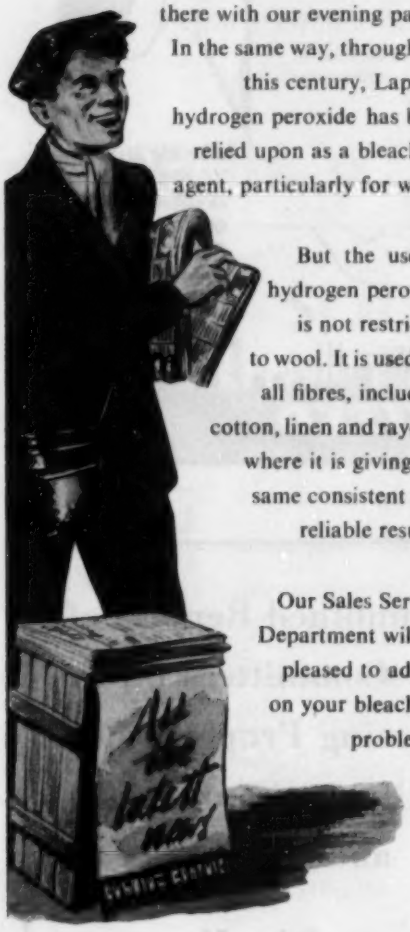

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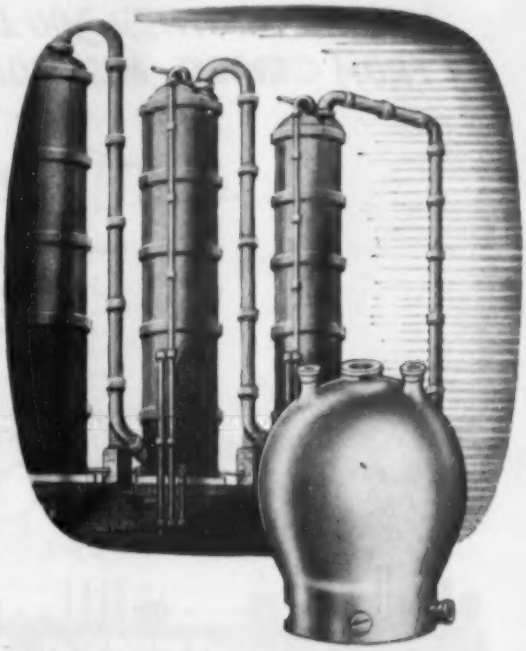

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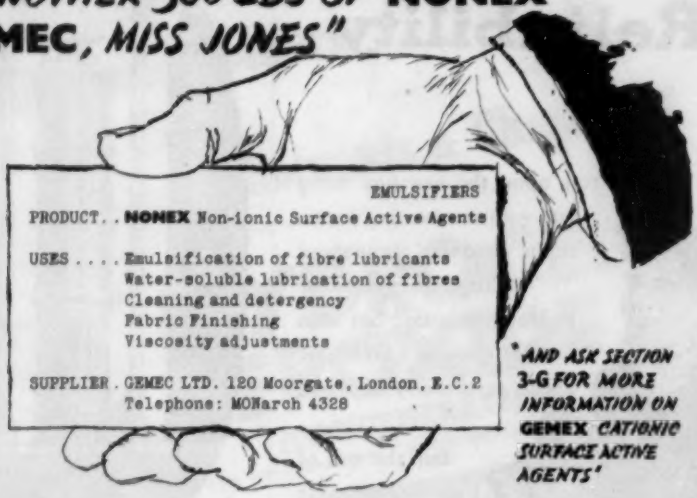

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